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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Photoelectric Methods in Analytical Chemistry

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PHOTOELECTRIC photometry has been an established branch of applied physics for half a century. The comparatively recent application of these methods to chemical problems has been very useful to the analyst, the physical chemist, and the biochemist. The best resources of optics and electronics are required in this field and abundant literature is widely scattered in numerous journals and monographs. In this review the writer has attempted to epitomize the more important facts and methods which are essential in chemical applications. Particular stress is placed upon the number of excellent monographs in the fields of optics and electronics. (These are collected ahead of the rest of the bibliography and referred to by letters in the body of the paper. Specific references in a monograph contain the page number; thus, *N*, p. 245, refers to page 245 of the monograph by Henny.) They afford instrumental and theoretical approaches which are largely untouched.

### Photometry and Colorimetry

The terms "colorimetry," "the colorimeter," and "colorimetric analysis" all suggest to the chemist definite concepts as familiar as the balance or other tools of the analytical laboratory. The physicist reserves these terms for those means of specifying color or for the measurement of color stimuli (*L, M, 71*). His terminology is undoubtedly correct and although a conservative estimate would indicate the present use of about 25,000 "colorimeters" in this country alone, the chemist will probably have to define his concepts more clearly.

To state the problem more definitely, it may be resolved into two categories:

1. The measurements are to describe the color of a system in unambiguous, reproducible terms. The problem might be to define the color of a dyed fabric, an oil sample, an impure organic compound, or a natural product. This is a true colorimetric problem in the sense of the physicist's definition.

Its solution demands a complete spectrophotometric analysis, or abridged methods in terms of trichromatic coefficients either of which may be reduced to the standard I. C. I. observer. The necessary data may be obtained either visually or photoelectrically. The complete treatment of this question is beyond the scope of this review; the best statement and approach to date are given by Gibson (*71*).

2. The measurements are to furnish information on the concentration of a colored substance, or the color produced by that substance when appropriate reagents are added. If there is a definite functional relationship between the intensity or "depth" of this color and the concentration, we shall be able to use such measurements for analytical purposes. In addition, such measurements may be used to study anomalies in the system itself, the existence of equilibria, or incompleteness of reaction and other physico-chemical aspects. If the system is measured with sensibly monochromatic light (filters) the process is then one of photometry.

Our main interest in this discussion will be the elaboration of problems encountered in the second category.

DEFINITIONS. In terms of Figure 1, let monochromatic light of intensity  $I_0$  strike the solution of thickness,  $t$ , the concentration of colored substance in this solution being  $c$ . The emergent intensity is  $I$ . According to Lambert-Beer's law [usually referred to in this form, although Lambert's work was anticipated by Bouguer in 1729 (see *M*, p. 24)] we have

$$I = I_0 10^{-kct}$$

If  $c$  is expressed in moles per liter and  $t$  in centimeters,  $k$  is the molecular extinction coefficient,  $I/I_0$  is the transmission,  $T$ , and  $\log_{10} I_0/I = E$  (the extinction). It follows that  $E = kct$  and  $-\log T = E$ .

Corrections for reflection at the surface of the liquid or the container are neglected, as most instruments contain comparison cells with pure solvent or standard solution. In the Duboscq colorimeter the depths of two solutions are varied until a match is obtained, under which condition

$$E_1 = E_2 \\ kc_1t_1 = kc_2t_2$$

or

from which

$$\frac{c_1}{c_2} = \frac{t_2}{t_1}$$

If monochromatic light is used, the above procedure is a truly photometric matching and will be rigorous to the extent that Beer's law is obeyed by the system. Usually, how-

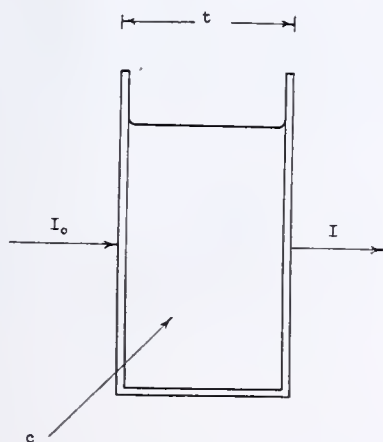


FIGURE 1  
 $\log_{10} I_0/I = kct = E$



ever, white light is employed and the conditions are not as rigorously defined as implied by the above equations. Nevertheless, over a limited concentration range, the thickness and respective concentrations are inversely related.

### Photoelectric Methods

The substitution of photocells for the eye has been accomplished in a number of ways. It is advisable to classify them and discuss each in turn.

In general it may be said that the adaptation of photocells to existing visual instruments is poor practice and wholly inadvisable. The uninitiated are inclined to place a photocell at the ocular of a microscope, spectrometer, refractometer, or "colorimeter" and then expect extraordinary results. The optics of these instruments are designed to accommodate the optical properties of the human eye and the available light is by no means most efficiently utilized by a photocell put in place of the eye (*M*, p. 422).

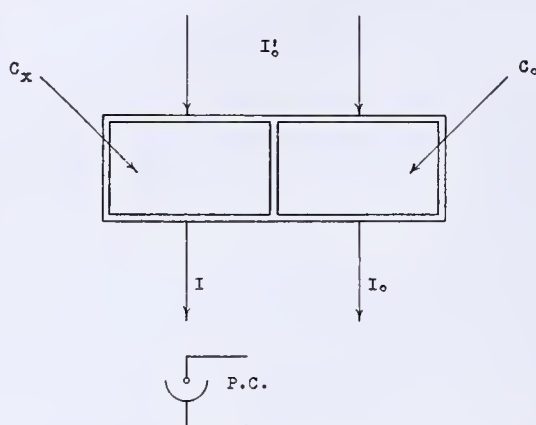


FIGURE 2. PHOTOMETRIC COMPARISON WITH PURE SOLVENT

Photoelectric methods are so attractive, and have offered so much promise of high precision and relief from fatiguing effort, that they have often been seized upon and utilized with little regard for sound principle. Little ordered progress can result from the use of instruments that require empirical calibration for each substance that is to be determined and over the entire concentration range. We expect our balances, refractometers, polarimeters, and potentiometers to yield direct measurements in terms of grams, refractive index, rotation in degrees, and potential differences in volts directly, with no particular reference to any substance. We insist upon a definite functional relationship (preferably direct) between the instrumental indication and the property in question. This is not too much to expect of a photoelectric photometer.

The ideal instrument would respond to any region of the visible spectrum with equal precision, indicating transmission or the extinction. The source would be monochromatic, so that the extinction would be a linear function of the concentration for any system which obeys Beer's law. No commercial instrument fulfilling these requirements has been offered. It is true that Hardy's photoelectric spectrophotometer does satisfy these requirements, but this instrument was designed for the vastly more complex problem of color analysis (true colorimetry) and its cost is naturally greater than the simplicity of our problem warrants. Many systems, including commercially available instruments, have been suggested which approach the specification. Others have been recommended in which the sole criterion of success is the author's ability to analyze a given substance under rigorously standardized conditions.

In general, it is preferable to effect a photometric match or balance and use the photocell merely to indicate this state.

On the other hand, it may be desirable to use the photocurrent as a measure of the unbalance, in which case it is necessary to have constant assurance that the photocell responds linearly with the light intensity.

**SINGLE-CELL METHODS.** A. If we illuminate a rectangular cell, containing in one compartment pure solvent,  $c = 0$ , and in the other compartment a solution of concentration  $C_x$ , with a parallel beam of monochromatic light, the light which strikes the photocell may be called  $I_0$  when  $c = 0$  is in the path. Upon substitution of the solution the beam will be reduced to intensity  $I$ . If the photocell response is linear, the respective photocurrents will measure  $I/I_0$  which is the transmission, or  $\log I_0/I$  gives the extinction,  $E$  (Figure 2).

This principle requires (1) constancy of the light source during the interval required to interchange the absorption cells, (2) linear response of the photocell, and (3) stability of the circuit used to measure the photoelectric current. An alternative procedure, which eliminates requirement 2, is to decrease  $I_0$  by introducing a compensating wedge, variable aperture, or polarizing equipment, until the response is identical for the two absorption cells.

The method has often been criticized by proponents of double photocell circuits, but very precise results have been obtained which show unquestionable reliability (85, 142, 144, 175).

**B. Flicker Methods.** A single photocell is used and a homogeneous beam is directed alternately through the solution and solvent by a rotating or vibrating shutter, (*B*; *I*, p. 200; 184), total reflecting prism (*K*, 2), or a mirror or rotating Rochon prism. The transition from one medium to the other must be smooth with no intervening dark period. Compensation is effected in the reference system until the emergent beams striking the photocell are of equal intensity. Any unbalance will give rise to a pulsating photocurrent. With or without amplification this pulsating current can be detected by short-period electrometers or galvanometers (*D*, p. 169), or the latter may be fed with the photocurrent after it has passed through a commutator which is driven synchronously with the scanning device (*X*, p. 228; 184). A tuned amplifier with telephone, or bridge-balance indicator may be used.

It is difficult to set any upper limit for the precision of this method. It is undoubtedly set by the optical refinements of the instrument. In any projected design it is wise to keep in mind the recommendations of Hardy (*M*, p. 294).

The two beams under comparison must have the same spectral quality and state of polarization.

The same area of the active surface of the cell must be illuminated at the same angle by both beams in rapid succession.

The transition from one beam to the other must take place without an intervening dark period.

**TWO-CELL METHODS.** The use of two photocells in some sort of balanced circuit has been used extensively (48, 78, 118, 132, 137, 140, 173, 180, 226, 229, 236). The method has the advantage of high differential sensitivity, in that only differences in intensity are measured. If properly designed, an instrument of this kind will compensate for variations in the light source. This is a very useful characteristic but it is by no means assured by the mere fact that two cells are used. As will be shown, some twin-cell circuits are definitely more unreliable and unstable than substitution methods employing a single cell.

This principle may be utilized in several ways:

1. The two photocells are illuminated from a common source, preferably monochromatic, and solution and solvent are placed in the respective beams. Assuming that the cells were initially adjusted for equal response, the net response will now be a measure of the absorption due to the solution (78, 118, 137, 140). Successful operation requires (a) linear response of both photo-



cells; (b) identical color sensitivity for the two cells, if white light is used. This is not important if monochromatic light is used, provided condition (a) is satisfied.

2. The above arrangement is used, but optical compensation is effected in the beam passing through the solvent. When the net response of the photocells is reduced to zero, the amount of light absorption is obtained in terms of the compensating device.

Linearity of response of both cells is still required unless compensation is effected in the absorbing branch (intensity increased to the same extent that the solution decreases it). Requirement (b) in the preceding method holds equally in this case.

3. The optical arrangement is similar to that of a Duboseq colorimeter, and the principle, that concentration and solution depth are inversely related, is employed (11, 77). Two photocells intercept the respective beams (preferably monochromatic) and the depth of one solution is varied until standard and unknown transmit equally, as indicated by a net photocurrent of zero. There are many commendable features in this method. For a limited concentration range, the demands upon strict monochromaticity of the source are less than in other methods. However, the optical design of the instrument presents great difficulties. The beams passing through the long variable layers must be strictly parallel and adequate stops must be provided to eliminate stray or reflected light. For this reason, existing visual instruments of this type cannot be converted to the photoelectric equivalent with any degree of success. The best criterion of successful design is the ability to secure reproducible settings which are independent of the total cup depth.

In all balanced arrangements, "reasonably" monochromatic light must be used if any simple physical interpretation of the results is desired. Similarly, when compensation is effected in the comparison beam, the functional relationship between the compensator and the quantity which is being measured should be known. For example, a nonselective wedge, if carefully made, will change the light intensity logarithmically with linear displacement, and under this condition its displacement will be a linear function of the concentration of any colored substance that obeys Beer's law. One instrument which used a white light source and an arbitrary slit mechanism for compensation actually reached the commercial production stage. It was beautifully made by a well-known company. The instrumental indications bore no recognizable relationship to the concentration; indeed, they were even irregular but withal highly reproducible.

The enormous burden of point-by-point calibration rendered it valueless for general utility.

Where precise results in absolute terms are desired the compensation method is preferable. Under these conditions fluctuations of the light source are of little consequence.

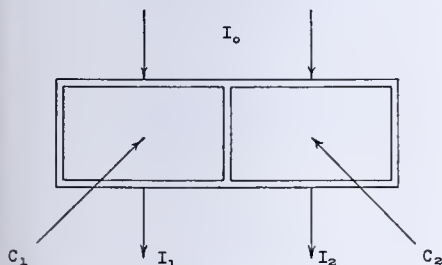


FIGURE 3. PHOTOMETRIC COMPARISON WITH STANDARD SOLUTION  
 $C_1/C_2 = \log I_1/\log I_2$

Since all photoelectric methods possess the inherent possibility of continuous indication and eventually automatic registration or control, it is of interest to see to what extent direct measurement of the photocurrent will be reliable.

Some generalization of this procedure may be of interest. For work of the highest precision it is advantageous to compare an unknown solution with one of identical nature but of a known concentration, preferably of the order of magnitude of the unknown. The results may be expected to be somewhat more accurate than a comparison with pure solvent, because the extinction coefficient can be independent of the concentration only if the light is strictly monochromatic. In general, if the main spectral line is accompanied by  $n$  other lines, for each of which the solution exhibits a char-

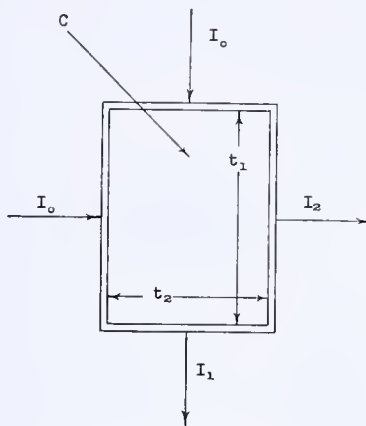


FIGURE 4. PHOTOMETRIC COMPARISON AT TWO THICKNESSES  
Without reference solution  
 $C = 1/(t_1 - t_2) \times \log I_2/I_1$

acteristic extinction coefficient, then the total extinction will be given by (85, 107):

$$E = \log \frac{I_0}{I} = \log \frac{\sum_0^n I_n}{\sum_0^n I_n 10^{-\epsilon_n c d}} = \bar{\epsilon} c d$$

where  $\bar{\epsilon}$  represents the average extinction coefficient for the heterogeneous light. Of course, the magnitude of this error also depends upon the nature of the solution. For a gray (neutral) colored solution

the error would be zero ( $\epsilon = \text{constant}$ , independent of  $\lambda$ ); for one with a sharp absorption band it might be very considerable, especially if one worked along the steep sides of the band.

This all implies that relative measurements of concentration can be made more precisely than an absolute measurement of the extinction coefficient. Table I, taken from Kortüm's paper (107), illustrates a case in which the extinction coefficient for a given system could be determined to no better than  $\pm 0.5$  per cent, whereas the concentration of a single solution compared with a known solution of the same order of magnitude could be determined to within  $\pm 0.02$  per cent.

TABLE I. CONCENTRATION MEASUREMENTS

( $C_s = 8.892 \times 10^{-6}$  mole per liter;  $d_s = 1.0917$  cm.;  $d_x = 1.9944$  cm.)

$C_x$ Mole/liter
$4.982 \times 10^{-6}$
4.980
4.979
4.979
4.980
4.978
Av. $4.980 \times 10^{-6} \pm 0.001$

This advantage may be realized in practice for any of the methods discussed above by substituting a standard solution for the solvent. Under these conditions the respective intensities emerging from unknown solution and standard solution (Figure 3) will be given by

$$\frac{C_x}{C_s} = \frac{\log I_x}{\log I_s}$$

An alternative scheme, which the writer has not seen described, would seem to offer some advantages. The unknown solution is contained in a rectangular absorption cell, and is viewed alternately through one side (Figure 4) (thickness of layer =  $t_1$ ) and then through the other side (thickness of layer =  $t_2$ ) either by rotating the cell through exactly  $90^\circ$  or by a suitable arrangement of prisms in the optical train. For the two positions we get:

$$\begin{aligned} \log I_0 &= kCt_1 + \log I_1 \\ \log I_0 &= kCt_2 + \log I_2 \end{aligned}$$

or

$$kCt_1 + \log I_1 = kCt_2 + \log I_2$$

and

$$C = \frac{1}{k(t_1 - t_2)} \log \frac{I_2}{I_1}$$



Now let

$$t_1 > t_2$$

then

$$I_2 \geq I_1$$

Further simplification is possible in practice, since the instrumental reading may be set equal to 100 for  $I_1$ ; then

$$c = \frac{1}{k(t_1 - t_2)} \log \frac{I_2}{I_1} = \frac{1}{kd} \log (0.01 I_2)$$

where

$$d = (t_1 - t_2)$$

### Photoelectric Cells

In modern instruments practically only two types of photocells are employed: the high-vacuum cell and the barrier-layer type. Special forms for particular problems will be mentioned later.

**VACUUM PHOTOCELL.** A highly evacuated cell with a composite cesium cathode may be taken as typical of this class. For a central anode cell we may discuss the characteristics in terms of Figure 5.

The cell is illuminated with light of intensity  $I$ , and under the influence of the applied potential,  $E$ , an electron current,  $i$ , flows through the load,  $R$ . Here  $R$  may represent an appropriate galvanometer or the input resistor of an amplifier. For constant illumination current  $i$  will increase with applied potential  $E$  as shown in Figure 6, indicating the saturation characteristic above a certain potential. For successively higher intensities similar curves are obtained ( $I_2, I_3, I_4$ , etc.). At very high intensities true saturation is not attained and this is commonly observed with central anode cells. Most commercial cells are of this type. Their total output is greater than cells of the central cathode type which give saturation currents with nearly zero applied potential (*O*, p. 422; 91). It follows that for precise photometry some minimum potential,  $E_m$ , must be applied across the cell in order that saturation currents may be obtained for all intensities that are likely to be encountered. If we now plot the corresponding saturation currents against the corresponding light intensities a straight line should result (Figure 7). Returning to Figure 5 we note that the potential across the cell is

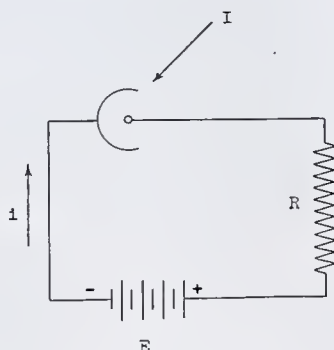


FIGURE 5. VACUUM PHOTOCELL

always less than  $E$ , by an amount equal to the voltage drop across  $R$ . In other words

$$E_c = E - Ri \quad (1)$$

This is especially important where amplification is used, for in this case the coupling resistor is usually chosen as high as possible ( $R < 50$  megohms). Care must be exercised that the resulting  $Ri$  drop is not too large, thus bringing the potential

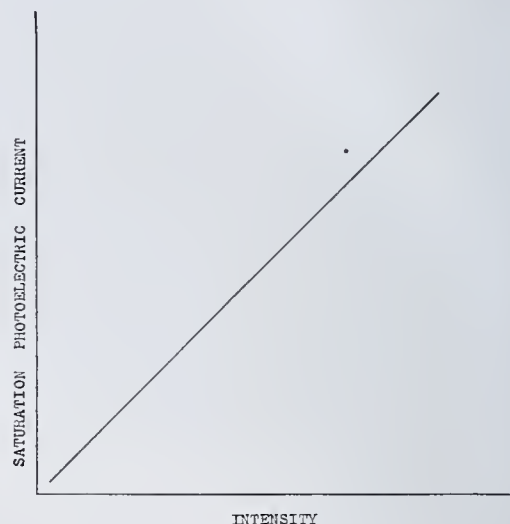


FIGURE 7

across the cell to a value below the minimal  $E_m$ . A conservative choice in  $E$  will be 10 per cent in excess of  $E_m$  after the above correction has been calculated. An excessively high potential is undesirable because there can be no gain in response but only increasing contribution to leakage currents.

**Color Sensitivity.** The response of a vacuum photocell to different regions of the spectrum depends upon the nature of the cathode surface and its treatment during manufacture (*F*, p. 161). Since most cells which are manufactured are used in sound-picture installations or for industrial control work, and are illuminated by incandescent lamp sources, they are purposely treated to accentuate the response to long wave lengths in order to utilize most efficiently the radiation from such sources. This is a decided disadvantage for colorimetric work; indeed, most of the infrared from such sources must be screened off by appropriate filters.

**Fatigue and Nonlinearity of Response.** There is little information available on the reliability of modern photocells. We have inherited many prejudices from the early days when cells were individually constructed in the laboratory. They undoubtedly bear little resemblance to the semiautomatic production of present-day cells. Some widely quoted papers (*B*, 92) give detailed information on the eccentricities of the photocell but neglect one very important point—i. e., the characteristics of the light source which is used in such tests.

In general it is advisable to use null or rapid substitution methods of photometry in which the cell is merely used as an indicator of photometric balance. Nevertheless it would be interesting to know just how reliable a good cell can be. It turns out that a photocell might better be used to study the constancy of a light source than for the converse test of cell stability or linearity. Simple considerations show why this is so. Let us imagine a vacuum cell to be illuminated with the unfiltered radiation from a 6-volt automobile lamp. Let  $V$  designate the lamp voltage and  $I$  the resultant photocurrent. Over a very wide range the empirical relationship (Equation 2) holds (144).

$$I = kV^n \quad (2)$$

The constant,  $n$ , has a value between 3 and 4. In other words, if we expect to reproduce the photocurrent,  $I$ , to within  $\pm 0.1$  per cent, the lamp voltage must not vary by more

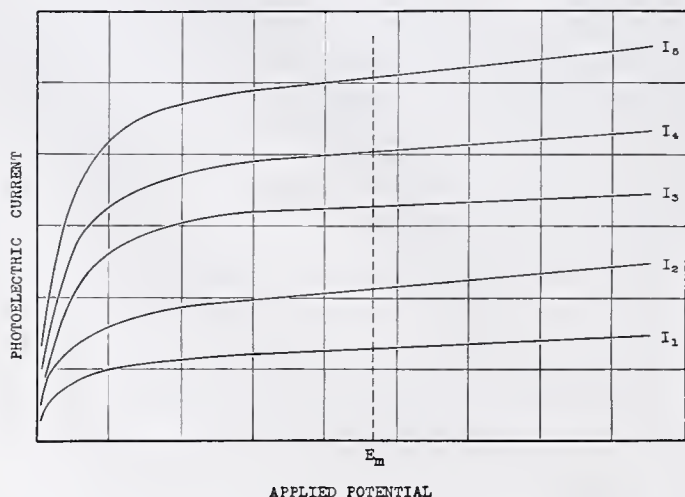


FIGURE 6. SATURATION CHARACTERISTICS OF A CENTRAL-ANODE VACUUM PHOTOCELL

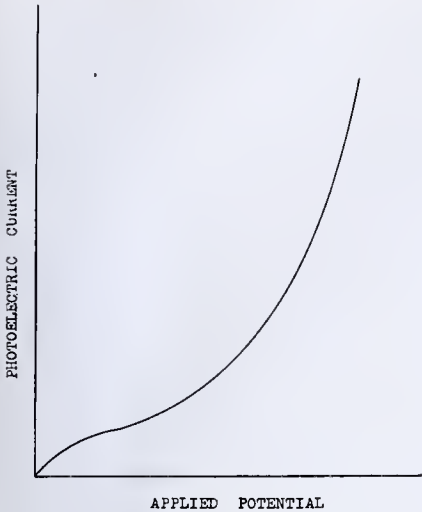


FIGURE 8. CHARACTERISTIC OF GAS-FILLED PHOTOCELL

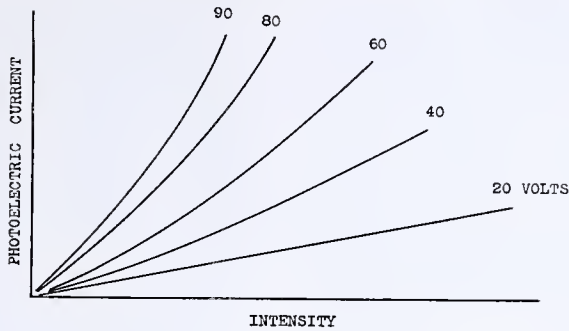


FIGURE 9. INTENSITY-CURRENT CURVES FOR GAS-FILLED PHOTOCELL AS A FUNCTION OF APPLIED POTENTIAL

than a few millivolts. Even if such a lamp is operated from storage batteries on the optimum portion of their discharge curve, this constancy will not be obtainable for more than a few seconds at a time. Any statements made without an exact statement of the condition of the source are therefore pointless. Some significant and interesting life tests on vacuum cells have been reported (*I*, p. 36). The response of several cells was automatically recorded for a period of 12,000 hours, under sensibly constant illumination. Whatever variations in photocurrent did arise, were common to all the cells and undoubtedly arose from temporary fluctuations in the common source.

It is generally agreed that the strict proportionality between photocurrent and light intensity is a fundamental law of photoelectricity, but its realization in practice demands a carefully designed and constructed cell (*O*, p. 32).

**Gas-Filled Cells.** The sensitivity of the cell described above may be increased greatly by admitting a small amount of rare gas. Argon at about 0.2-mm. pressure is usually used. Ionization currents are superimposed on the primary photoelectric current and the response may be increased tenfold. Figure 8 shows typical characteristics of a gas-filled cell. Very few modern schemes of photometry utilize the gas-filled cell for the following reasons:

Linearity of response is approached as the potential applied to the cell is reduced, and is attained near the ionization potential of the gas. Under these conditions the cell is really behaving like a vacuum cell and all the advantages of amplification by ionization have disappeared (Figure 9).

If modulated light is used, gas cells show a definite lag in response.

High-gain amplifiers with adequate stability are available which entirely offset the slight gain obtained by the use of gas-filled cells.

**Special Cells.** The high-vacuum cell is available in many sizes and shapes, with a choice of cathode and envelope material (*F*, p. 161). Cells sensitive to the ultraviolet are commercially available. Some of the products of television research will undoubtedly be available in the future; the multiplier tubes of Zworykin (239) and Farnsworth (*F*, p. 214) are notable examples. In these tubes the primary photoelectrons are made to collide with a sensitive sur-

face from which secondary electrons are emitted. This process may be repeated many times with a gain of 4 to 8 at each stage. A single multiplier phototube thus yields an output comparable with a cell-multistage amplifier combination with the added advantage that the ratio of signal to noise is increased approximately one thousand fold. Cells with split cathodes and multiple cathodes have been designed for special problems (*R. C. A.* 920). The iconoscope, a mosaic consisting of myriads of photoelements electronically scanned, is an integral part of one important method of television.

**BARRIER-LAYER CELLS.** The most recent addition to the family of light-sensitive devices is the barrier-layer cell, variously termed the dry-disk, blocking layer, photovoltaic, or Sperrschicht cell, or by trade names such as Photronic (Weston) or Photox (Westinghouse). The apparent, but deceptive, simplicity of these cells undoubtedly accounts for the recent interest which has arisen in many fields in the application of photoelectric methods. The recent monograph by Lange (*Q*) gives an excellent account of the discovery, development, and properties of these cells. The second volume deals with applications and instruments.

**Properties and Characteristics.** These cells consist essentially of a plate of copper or iron upon which a semiconducting layer of cuprous oxide or selenium is grown. The semiconductor is covered by a light-transmitting layer of metal—gold, platinum, copper, or lead—which serves as a collector electrode. Upon illumination through the transparent electrode an electron cur-

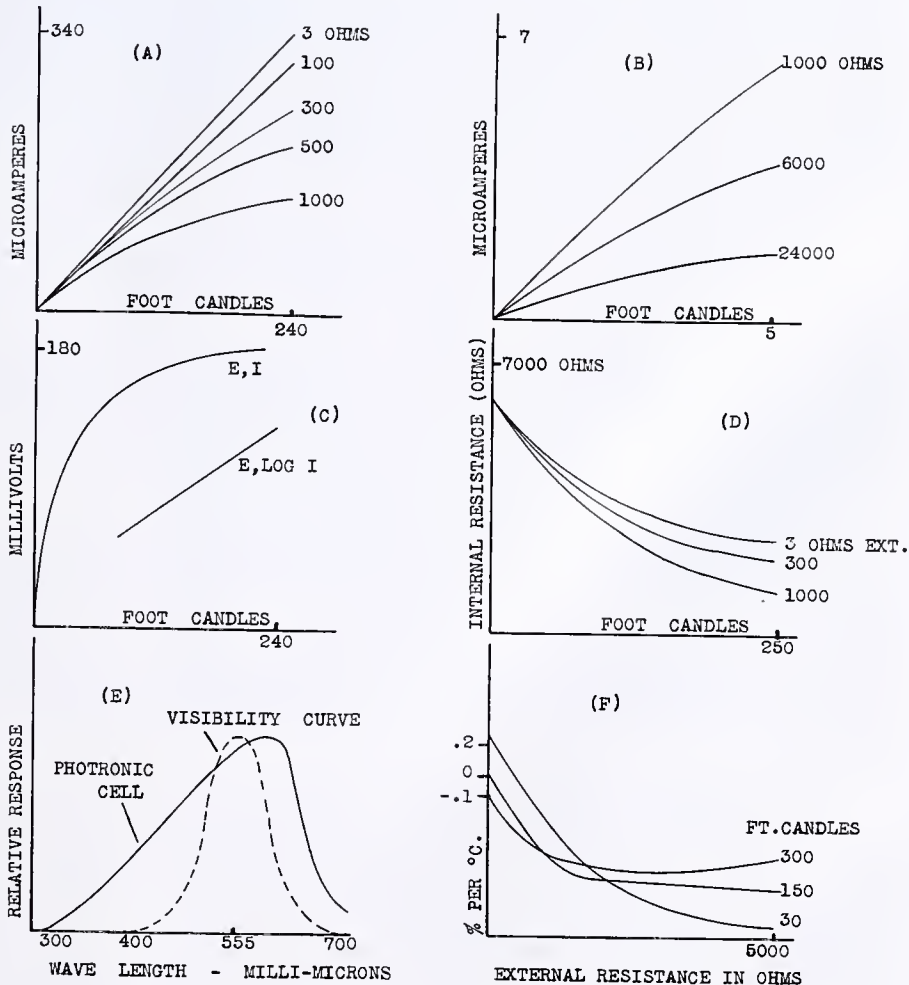


FIGURE 10. PHOTRONIC CELL CHARACTERISTICS



rent flows. In this type no auxiliary source of e. m. f. is required. For this reason Lange has termed these cells photoelements in analogy with galvanic elements. The more important characteristics are represented in Figure 10.

The photocurrent is very nearly directly proportional to the light intensity for low values of the external circuit resistance,  $R$  (Figure 10, *A* and *B*).

The open circuit e. m. f.-intensity relationship is shown in Figure 10, *C*. The linear relationship between  $E$  and  $\log I$  has interesting possibilities for colorimetry (146) and has been neglected or overlooked in American practice, although Lange (9) has accounted for it on theoretical grounds and shown that a formal analogy with the Nernst equation for a concentration cell predicts the observed phenomenon.

The "internal resistance" of the cell decreases with increasing illumination (Figure 10, *D*).

The temperature coefficient is complex and is a function of the external circuit resistance (Figure 10, *F*).

The spectral response extends from the x-ray region to about 1 to 1.2  $M$  in the infrared. The ordinary cell with a glass window exhibits a response curve as shown in Figure 10, *E*. Filters have been designed to adjust this response to approximate that of the average human eye (54, 55, 65, 153).

The average cell has an output of about 120 microamperes per lumen. The best high-vacuum cell of the photoemissive type yields 40 to 60 microamperes per lumen. For high levels of illumination robust instruments such as micro- or milliammeters may be used with barrier-layer cells. In direct sunlight 10 milliamperes have been obtained.

**Special Types.** For special applications, cells with a differential connection have been designed; a split cell for comparing two adjacent illuminated fields is available, as well as ocular eyepiece types which fit a microscope draw tube. Giant cells, consisting of a number of elements connected in parallel, are available (9).

**COMPARISON OF EMISSIVE AND BARRIER-LAYER TYPES.** It is important to keep in mind the relative advantages and limitations of each type of cell. There has been a tendency in some circles to regard the barrier-layer cell as vastly superior and simpler than the photoemissive type. This is by no means true, depending entirely upon the particular problem to be investigated. At very high levels of illumination the comparatively heavy currents furnished by a barrier-layer cell are impressive. However, in most photometric work the available radiation is feeble, especially if a monochromatic beam is employed. A rough comparison under these conditions will illustrate the point.

Suppose we consider a photonic cell of sensitivity 120 microamperes per lumen, which is receiving radiation of  $10^{-6}$  lumen. The current will be  $1.2 \times 10^{-10}$  ampere. A good cell of the emissive type (40 microamperes per lumen) under the same conditions will deliver  $4 \times 10^{-11}$  ampere. If we use galvanometers of appropriate characteristics and a sensitivity of  $10^{-10}$  ampere per millimeter, we shall obtain 1.2-mm. and 0.4-mm. deflection, respectively. In each case we shall be able to detect light, but in no sense can it be measured accurately. In the case of the photonic cell the dilemma is genuine because amplification is impossible, for assuming the load resistance to be 5,000 ohms, the potential drop available is only 0.6 microvolt. This is about the noise level of an amplifier, and while the effect would be detectable it could not be measured. In the case of the emissive type, amplification with a single, stabilized F. P. 54 tube would solve the problem. As will be shown later, a current of 25 microamperes could be obtained under the above conditions. Thus full-scale deflection could be obtained on a 0-25 microammeter. Assuming 100 scale divisions, the photocurrent could be measured with better than 1 per cent precision.

The barrier-layer cell yields relatively large currents at a low potential. The internal resistance is low and decreases with increasing illumination. The emissive type yields smaller currents, but it has a very high resistance. Since the load should match the impedance of the source, it is readily seen why the latter type is amenable to amplification.

**Amplifiers.** The vast literature of vacuum-tube theory and application is directed largely to its most important field,

communication. Nevertheless a number of monographs deal extensively with noncommunication uses ( $E$ ,  $F$ ,  $K$ ,  $N$ ,  $P$ ,  $R$ ,  $S$ ). A few of the more important considerations are discussed below.

Figure 11 illustrates a simple arrangement of photocell and triode which may serve for this discussion. The grid and plate potentials are adjusted to the rated values for the particular triode which is chosen. The photocell battery provides a potential high enough to produce saturation currents for the prevailing light intensities. Upon illumination the photocell will deliver a current,  $i$ , which flows through the high resistance,  $R$ , thereby producing a potential difference,  $Eg'$ , across its terminals. This will make the grid more negative with respect to the cathode and consequently the plate current will be reduced by an amount  $\Delta I$ . The magnitude of this change is governed by an important constant of the triode known as the mutual conductance,  $G_M$ . (The advent of multigrid tubes has necessitated a more specific designation,  $S_p$ , termed the grid-plate transconductance.) Its value is given by:

$$G_M = \left( \frac{\partial I_p}{\partial E_g} \right) E_p \quad (3)$$

It is expressed in units of reciprocal ohms  $\times 10^{-6}$  and designated micromhos. For a given tube the value depends upon the plate and grid potentials. An average value suitable for the circuit of Figure 11 is 1,000 micromhos. This means that a change in  $Eg'$  of 1 volt will produce a change in plate current of  $\Delta I_p = 1$  milliampere.

Let us suppose that the triode has this value for  $G_M$ . If  $R$  is equal to 10 megohms, then a photocurrent of  $10^{-7}$  will produce a change of plate current of 1 milliampere. The gain is therefore  $10^{-3}/10^{-7} = 10^4$  or ten thousand fold. This is a very conservative case and by no means approaches the limit to which this process can be extended. The factors which limit indefinite gain are as follows:

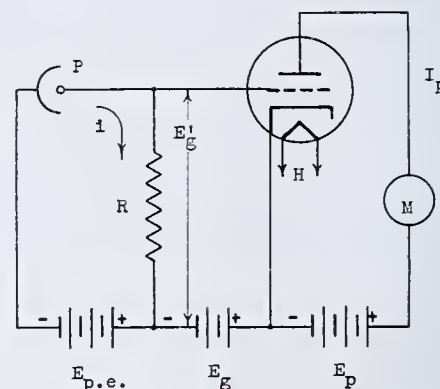


FIGURE 11. TRIODE-PHOTOCELL CIRCUIT

**Grid Currents.** While the grid exerts its control primarily electrostatically, yet in high-gain tubes with large values of  $G_M$ , the grid does collect some electrons and a finite current flows in the grid circuit. It is obvious that the magnitude of this grid current limits the small currents which can be measured in the input circuit.

**Insulation.** Leakage currents between tube elements, over

the glass envelope and at socket terminals, set limits to the gain that can be realized in practice.

**Ionization Currents.** Although modern tubes are very highly evacuated, there is sufficient gas present to furnish positive ion currents. If the potentials applied to the tube elements are reduced to low values (below the ionization potentials of the residual gases) this disturbance can be eliminated. This entails a very considerable reduction in gain but it can be overcome, if necessary, by succeeding stages of amplification of the conventional type.

**Photoelectrons and Soft X-Rays.** Photoelectrons may be emitted from the metal tube elements because of light from the filament or indirectly heated cathode, and similar disturbances may arise from the soft x-rays emitted by bombardment of the plate by electrons.

Special electrometer tubes have been developed in which systematic studies of the above-mentioned difficulties have established the correct design. The General Electric FP. 54 tube was the first of this class (131). In appropriate circuits, currents as



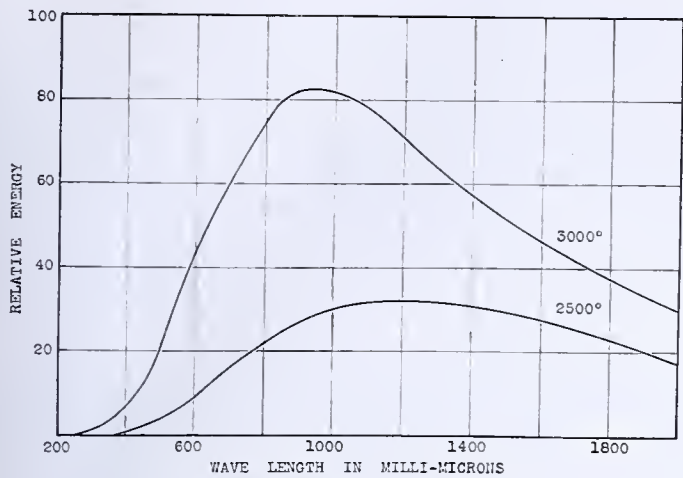


FIGURE 12. ENERGY DISTRIBUTION OF INCANDESCENT SOURCE

low as 30 electrons per second have been measured (41) with this tube. Other electrometer tubes are the Western Electric Company's D-96475 and the R. C. A. A-154. Westinghouse manufactures semielectrometer tubes of the inverted triode type, the DRH-506 and DRH-507. A further compromise between commercial and electrometer tubes is afforded by their RJ-550 and RJ-553.

In general, it should be emphasized that many commercial triodes if operated at subnormal voltages will approach electrometer tube performance. The low gain may be made up by subsequent stages of amplification in the conventional manner.

Light Sources

**TUNGSTEN LAMPS.** The tungsten incandescent lamp is one of the most convenient and widely used sources for photoelectric measurements. The energy distribution throughout the spectrum is not ideal for the purpose, as may be seen from Figure 12, particularly if it is used with a red-sensitive cesium cell. The effect of this energy distribution is best illustrated by noting the effective response of a cesium (blue response) cell when used with this type of illuminant (Figure 13). The importance of these simple considerations cannot be overemphasized. If we keep in mind that most of the energy is in the infrared and very little at the shorter wave lengths it will be seen that all sensitivity curves and effective filter transmission curves may be displaced considerably when they are used with an incandescent source.

TABLE II. VALUES OF *n*

Characteristic	Value of <i>n</i>	
	<i>W</i> , vacuum	<i>W</i> , gas-filled
Lumens, volts	3.5	3.6
Watts, volts	1.6	1.5
Lumens per watt, volts	1.9	2.1
Lamp life, lumens per watt	-7.0	-6.8

A general expression similar to Equation 2 may be used to define the characteristics of tungsten lamps (61). Thus

$$\frac{X_1}{X_2} = \left(\frac{V_1}{V_2}\right)^n$$

The best-known values for exponent *n* for some properties as a function of lamp voltage, *V*, are given in Table II.

Lamp-life ratings would seem to be primarily of economic interest, but actually it is advantageous to choose a light source somewhat larger than required and operate it at slightly subnormal voltage. Replacement and possibly

necessary recalibration are therefore less frequent. Industrial experience has indicated that this practice applies to electronic equipment in general, and satisfactory performance after 20,000 hours' use has been reported. On the other hand, moderate overloading enhances the brilliance and occasions a favorable shift of energy distribution. This is exemplified by the photoflood lamps used in photography. It is obvious that several factors will govern the choice of operating conditions.

Low-voltage lamps may be operated from storage batteries or transformers. For the former, a well-charged battery should be used and only over the optimum portion of the discharge curve. The use of a voltmeter across the lamp terminals is pointless except as a rough indication of the operating voltage. Unless a suppressed zero instrument is available it can be seen from Equation 2 that the photocurrent is a much more sensitive indicator of lamp conditions than a voltmeter. If it is necessary to know the lamp voltage, a volt box in combination with a simple potentiometer reading to ±0.1 millivolt will suffice.

Operation from a step-down transformer is very convenient and fairly constant illumination can be obtained by special

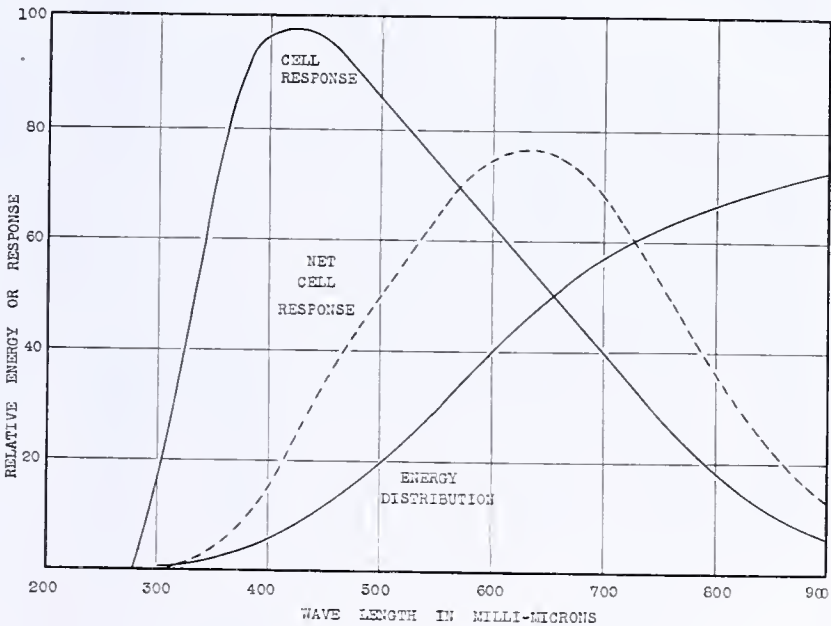


FIGURE 13. EFFECT OF ENERGY DISTRIBUTION OF THE SOURCE UPON PHOTOCELL RESPONSE

transformers of the three-legged saturation type (Ward Leonard Mfg. Co., Mt. Vernon, N. Y.). In all cases of alternating current operation an appreciable modulation of the light occurs, owing to slight cooling of the filament on each half cycle. The photocurrent will be partially modulated at twice the line frequency (usually 120 cycles). This is important in some cases, especially where amplification is employed.

**MERCURY ARC.** The modern mercury arc is a most convenient source, yielding several strong groups of lines in the visible spectrum.

	Å.
Yellow	5791; 5770
Green	5461
Blue	4358; 4348, 4339
Violet	4079; 4047
Near ultraviolet	3663.3; 3662.8; 3655; 3650

The intensity of these lines as a function of lamp wattage was carefully investigated by Kűch and Retschinsky and others (58, 59, 60, 112, 166). The absolute intensities as well as the relative values depend upon many factors such as lamp



dimensions, current, voltage, ambient temperature, etc. Individual lines can be isolated with reasonable purity by filter combinations. The ordinary mercury pool-cathode type is subject to considerable flicker even in a well-ballasted circuit. If a high-voltage storage battery is available, the lamp may be operated steadily enough to permit measurements by the substitution method. In photometric methods of the balanced or null type, the flicker is of no consequence, provided that there is no asymmetric displacement of the source.

The rare gas-mercury vapor discharge tubes are very stable, owing to the absence of liquid mercury. The intensity varies almost directly with the current through the lamp. Owing to the rare gas excitation, the mercury resonance lines are favored and the visible lines are relatively weak. As exemplified by the Hanovia S2537 lamp, about 40 per cent of the radiant energy is emitted by the first resonance line—2537 Å.—the tube is feebly luminous and not uncomfortably warm. It is primarily suited for work in the ultraviolet.

Vacuum tube-excited lamps show considerable promise and have been made with high luminous efficiency (*F*, p. 182). The radiation is practically completely modulated at the prevailing frequency; the modulation is limited chiefly by the de-ionization time.

Rare gas discharge tubes containing argon, neon, or helium, provided with a hot cathode, afford brilliant sources with an abundance of lines. The intensity varies practically linearly with the current through the lamp. These sources will undoubtedly become increasingly important as these newer illuminants become more generally available.

**Stabilized Sources.** Most photometric methods are designed to eliminate the unavoidable flicker or secular variation of intensity of the source. Nevertheless, a perfectly steady source of light, preferably monochromatic, would be an extremely useful adjunct in photoelectric photometry. Some successful attempts in this direction include: lamp excited by a generator driven by a synchronous motor; lamp excited by a generator with vacuum-tube field control (*F*, *K*, *N*, *R*); lamp current controlled by a saturable reactor (thyatron control, *F*, *K*, *N*, *R*); and current stabilized by a power tube shunt (87).

These methods are characterized by an attempt to furnish a very constant source of current. It is likely that photoelectric control of the source itself is more promising, inasmuch as the light intensity usually varies exponentially with the current or voltage.

### Monochromators and Filters

All but the crudest photoelectric measurements demand some approximation to monochromaticity of the light source. For the highest precision and work requiring information of a fundamental nature, spectral isolation, preferably with a double monochromator, is necessary. Naturally, considerable reduction in intensity accompanies this process. Stray or scattered radiation is an important factor; this can be avoided by supplementing the monochromator with filters or by using a second monochromator. It is beyond the scope of this review to discuss this subject in detail; it is dealt with in numerous papers and manufacturers' bulletins (*H*, *M*).

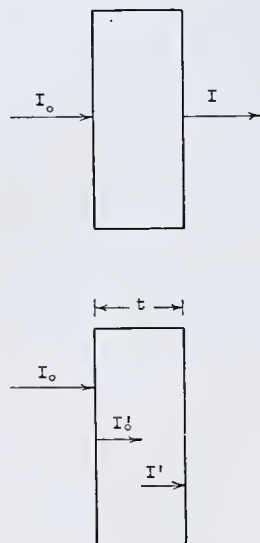


FIGURE 14. DEFINITION OF FILTER CONSTANTS

An excellent example of meticulous care in spectral isolation has been given recently by Hogness and his co-workers (84).

**FILTERS.** Aside from the fact that fundamental information about the light absorption of a system can be obtained only with monochromatic light, it is evident that greater sensitivity will be obtained if only that light which is most strongly absorbed is employed for photometry. The use of appropriate filters will solve most problems, but from this discussion of energy distribution in sources and the selectivity of cells it will be apparent that their choice requires some care. We may divide filters into several classes.

**Liquid or Solution Filters.** Appropriate colored solutions of reasonable stability are described in the literature (90). They are used in rectangular cells of optical glass. Heat-absorbing filters of this class are the common water cell or dilute copper chloride solution. (The use of these well-known adjuncts is burdened with the appearance of bubbles and for this reason heat-absorbing glass filters are gradually replacing them.) In general, this class of filter is used only when no glass filter of the desired transmission is obtainable.

**Glass Filters.** These are available in great variety, the Corning and Jena filters being the best known. Typical transmission values are available in bulletins of the Corning Glass Co., Schott, Jena, and also in handbooks (82, 89). The transmission,  $T$ , for a given wave length refers to the ratio of light intensity leaving the second surface to that incident upon the first surface. The transmittance,  $C_t$ , is the ratio of intensity incident upon the second surface to that leaving the first surface: In other words, it is the transmission corrected for surface losses (Figure 14). These are due primarily to nonselective reflection and usually amount to 4 per cent at each surface. Following the notation of Gage (65) we may relate these quantities to the thickness of the filter.

Let

- $T$  = transmission of the piece of glass
- $C$  = transmittance per mm. of glass
- $C_t$  = transmittance for  $t$  mm. of glass
- $t$  = thickness
- $\beta$  =  $\log_{10}$  transmittance for 1-mm. thickness.

Then from the above

$$T = 0.92 C_t$$

(due to 8 per cent loss by reflection) or

$$C_t = T/0.92$$

Since  $C_t = C^t$ ,  $\log_{10}$  transmittance =  $\log_{10} C_t = t$ , which may be written

$$\beta t = \log_{10}(T/0.92) = \log_{10} T - 0.0362$$

Gage (65) has given a typical example of how the thickness of two pieces of glass of known spectral transmission may be computed in order to reduce the response curve of a photonic

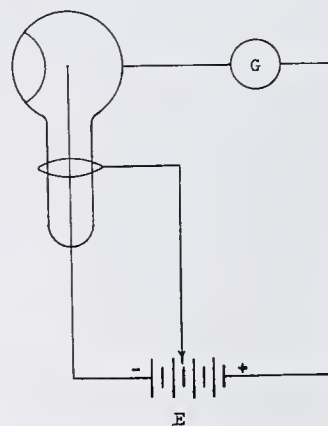


FIGURE 15. SIMPLE PHOTOMETER WITH VACUUM PHOTOCELL

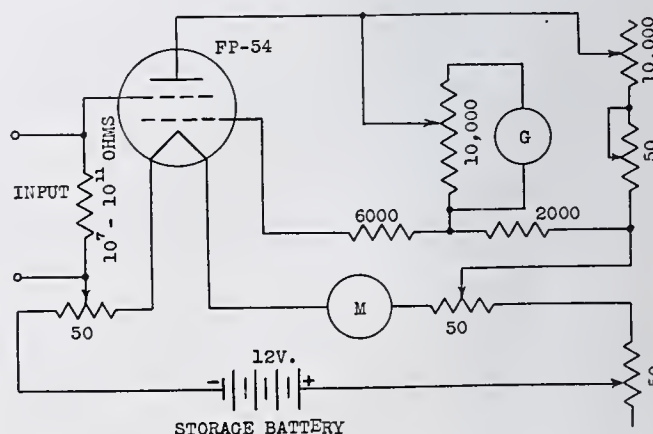


FIGURE 16. STABILIZED ELECTROMETER TUBE CIRCUIT  
Suitable for photoelectric measurements



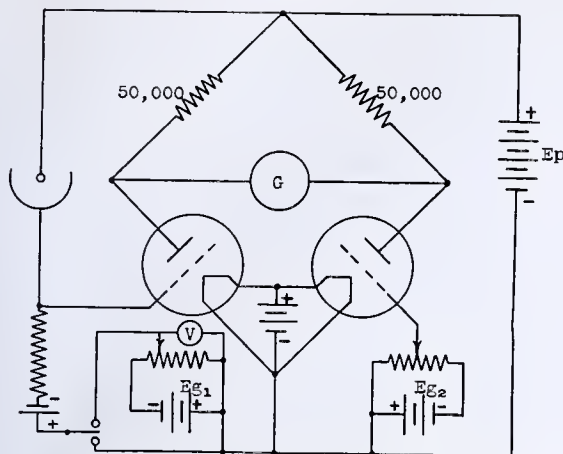


FIGURE 17. VACUUM-TUBE BRIDGE CIRCUIT FOR PHOTOELECTRIC PHOTOMETRY

cell to that of the average eye. For the more exacting problem of computing filters for use with a photocell such that the trichromatic coefficients may be obtained in terms directly reducible to the standard I. C. I. observer, Gibson (71) has prepared an excellent summary.

**Gelatin Filters.** Thin films of gelatin in which dyes have been incorporated provide very useful filters, usually mounted between plates of clear optical glass. The Wratten (43) filters are typical of this class and are widely used, especially in photography. They are usually more selective than glass filters but they must be handled with great care, especially with respect to overheating. Some of them lack permanence because of thermal and photochemical changes, although these limitations are clearly indicated by the manufacturers. In cases where their use is preferred, it is advisable to introduce the filter in a position most remote from the light source in order to minimize thermal effects. It must not be inferred that gelatin filters stand alone in their susceptibility to heat. Selenium glass filters and probably others are perceptibly affected by increase in temperature and this must be kept in mind at all times.

**CIRCUITS.** Some circuits are obviously straightforward and understandable; others have been recommended by chemists because they solved the problem in hand. Wherever possible, the writer has attempted to analyze and interpret them physically in order to evaluate their general utility.

**Photoemissive Type, A,** (for single-cell methods with vacuum photo cells). 1. For moderately high intensities the simple arrangement of Figure 15 is satisfactory. A guard ring is attached to the photocell as shown in order to minimize leakage. A galvanometer of sensitivity  $10^{-10}$  ampere per mm. is satisfactory. For some work an Ayrton shunt in the galvanometer circuit is very convenient. Its value should leave the galvanometer slightly underdamped. Another great convenience is to supplement the usual scale with a logarithmic scale (85). This simplifies the computation of extinction values.

2. The general aspects of amplification have been discussed. Figure 16 shows a typical stabilized circuit using an electrometer tube and a sensitive galvanometer (N, p. 91). The theory and design of stabilized circuits are discussed in several papers (42, 192, 214, 219).

3. The use of vacuum tubes in bridge circuits is exemplified by several examples. In Figure 17 two tubes form adjacent arms of a Wheatstone bridge. When the photocell is dark, the grid bias on the right-hand tube is adjusted until the bridge is balanced. Upon illumination of the photocell, the plate re-

sistance of the left-hand tube decreases and the bridge becomes unbalanced. Balance is then restored by changing the grid bias of this tube. The voltmeter, V, indicates a potential which is equal to the  $iR$  drop in the grid resistor. This, of course, is directly proportional to the photocurrent. In modern practice a twin triode would be used because the common heater and related factors would enhance the stability. Bridge circuits of this sort are less sensitive than the equivalent single-tube circuit, but they are more stable.

4. The 6F5 circuit shown in Figure 18 has been used extensively in the writer's laboratory (68). It is simply a vacuum-tube voltmeter with a convenient direct-reading bias adjustment. When the photocell is darkened, the zero bias is adjusted to give a standard plate current reading. When the cell is illuminated with light coming through the solvent,  $I_0$ , the dials of the potentiometer box are set at unity (1.0000) and the working current is adjusted until the standard plate current is again obtained. Now when the solution is interposed (intensity =  $I$ ) the potentiometer dial and slide wire are adjusted until the standard plate current is again obtained. The potentiometer now indicates the transmission directly. Since  $-\log T = kc$  these transmission values enable one to calculate the concentration. In addition, the working current may be measured very simply and can be admitted to the potentiometer in calculated amount for each type of determination (specific values of the extinction coefficient,  $k$ ).

5. For those methods in which two beams strike a single cell alternately (method B) alternating current amplification may be used for the pulsating unbalance-component. Figure 19 shows the connection of photocell cathode directly to the grid of the first tube. Low potentials are used on this tube in conformity with electrometer tube practice (M, p. 294). This tube may be followed by a multistage amplifier, terminating in the voltage coil of a wattmeter (N, p. 425) or a thyatron controller (N, p. 426; 80). For null indication the bridge balance indicator of Garman is well suited. It achieves a sensitivity of a few microvolts, by means of a single multi-electrode tube (66).

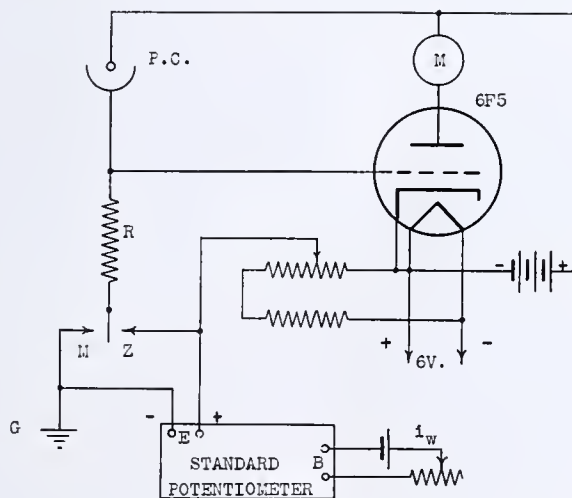


FIGURE 18. SENSITIVE VACUUM-TUBE VOLT-METER  
With precise input compensation for photoelectric photometry

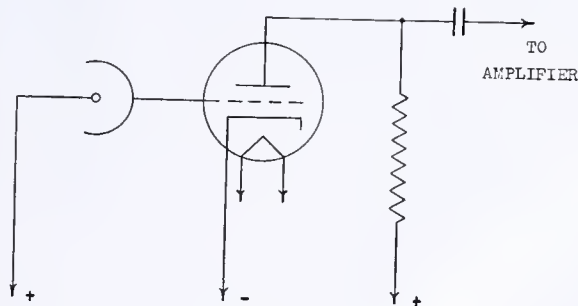


FIGURE 19. PHOTOCELL PREAMPLIFIER CONNECTION  
With differential sensitivity independent of illumination level

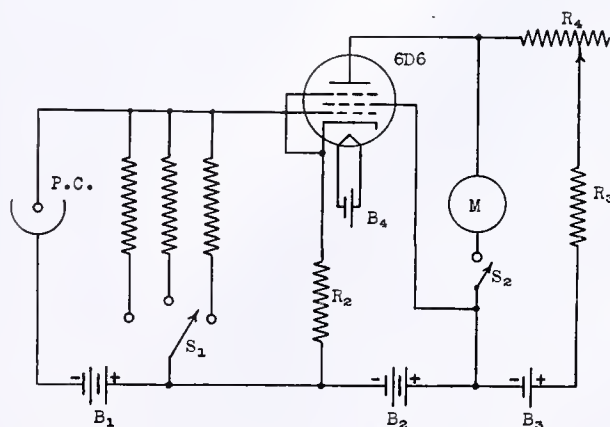


FIGURE 20. PHOTOMETER WITH LOGARITHMIC RESPONSE  
Linear in concentration units



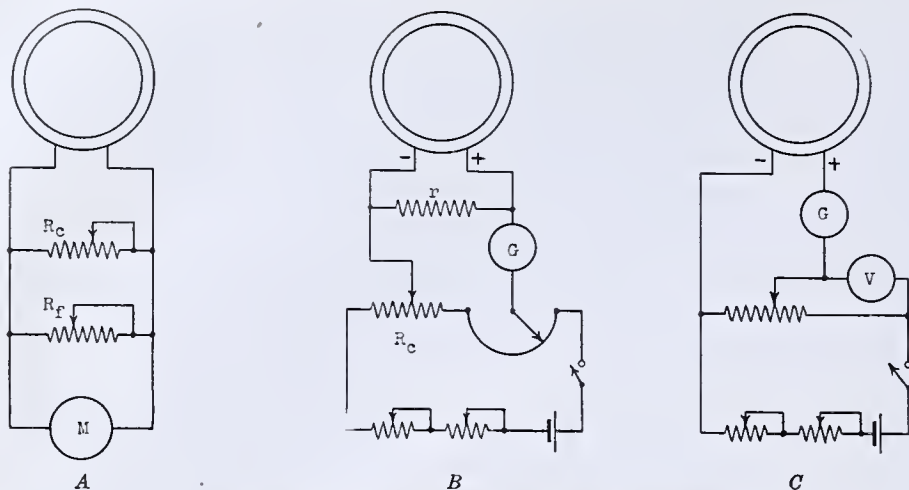


FIGURE 21. PHOTRONIC CELL PHOTOMETERS

- A. Measurement of short-circuit current  
 B. Potentiometric measurement of current  
 C. Measurement of open-circuit e. m. f.  
 Logarithmic response at high levels of illumination

6. Figure 20 is a direct-reading arrangement (concentration units). The 6D6 tube is of the remote cutoff type, and by a suitable choice of the cathode resistor,  $R_c$ , it is possible to make the plate current directly proportional to the logarithm of the input voltage (147). Since this voltage is proportional to the light intensity, the plate meter can be calibrated in concentration units directly. The normal component of the plate current must be balanced out, since the logarithmic relation cannot extend to zero plate current. This is an advantage, however; it is equivalent to a suppressed zero meter. A choice of grid resistors is available; indeed, these can be selected of such value that they stand in the ratio of the respective extinction coefficients of the various substances which are to be analyzed. A routine instrument would therefore bear a selector switch labeled Fe, Mn, Cr, Cu, etc., each representing an input resistor of the appropriate value to suit the extinction coefficient. The plate meter would bear a linear scale reading in micrograms or per cent of the desired constituent. A calibrated shunt would be necessary for the plate meter.

**Barrier-Layer Type, B.** 1. We have seen that the short-circuit current in this type is very nearly directly proportional to the light intensity, provided the external circuit resistance is low. The simplest arrangement consists of the cell connected to a low-resistance microammeter with two variable resistors of low and high resistance as shunts to provide coarse and fine adjustment of the current flowing through the meter (Figure 21). Suitable microammeters of low resistance are available, and recent improvements, such as new alloy steels for the permanent magnet and other innovations, are contributing to the solution of this problem of measuring small currents from a low potential source.

The tendency for these cells to "overshoot" must be kept in mind; it is imperative to measure the equilibrium value of the photocurrent.

By the substitution method, the transmittancy of a solution relative to pure solvent may be obtained by the ratio of the corresponding photocurrents. In instruments embodying this principle the meter is usually calibrated in 100 divisions, so that the transmission may be read directly. Logarithmic scales have been provided enabling one to read extinction values directly. The Kuder (5, 111) instrument contains a series of translucent scales arbitrarily engraved for direct reading of concentration. This is extremely convenient for rapid work but it would seem to place a great burden of responsibility on the manufacturer of such an instrument, in that any unwarranted changes in technique of preparing the solutions would render the scale useless.

2. A more flexible scheme is that shown in Figure 21, B. Resistor  $r$  must be low enough to allow photocurrents to flow which are directly proportional to the light intensity. The potential difference across  $r$  is measured by the simple slide-wire potentiometer. This is a conventional circuit in every respect. The galvanometer resistance should be low—i. e., the instrument should be chosen for high voltage-sensitivity. The slide wire will read per cent transmission directly if initially it is set at 100 when  $I_0$  is being measured.

3. If fairly high levels of illumination are available the logarithmic circuit of Figure 21, C, is useful. As shown previously, the open circuit e. m. f. of a barrier-layer cell is directly proportional to the logarithm of the light intensity. For the average cell this relationship prevails for potentials above 60

millivolts. The potentiometer circuit is essentially the Hildebrand arrangement commonly used in electrometric titrations, except for the position of the millivoltmeter. It is so chosen that the readings will increase with increasing concentration of the light-absorbing substance. For any colored substance which obeys Beer's law this circuit will give the concentration directly because of the logarithmic response.

**Balanced Circuits with Barrier-Layer Cells.** Circuit 1. The circuit shown in Figure 22 has often been used, but occasionally with the mistaken notion that it compensates for fluctuations in the light source. For the analysis of this and the following circuits we shall designate a common light source of intensity,  $I$ , which illuminates two essentially identical cells, 1 and 2. The light incident upon cell 1 passes through the sample of transmission  $T$ . The respective photocurrents,  $i_1$  and  $i_2$ , flow through the galvanometer in opposite directions. In this and the remaining cases, absolutely identical photo-cells are not necessary. It is merely assumed that each shall exhibit linear response over the prevailing light intensities and that they are initially adjusted (by virtue of position or the use of stops) for equal response. Slight differences in spectral response are usually of no importance, since most applications demand at least approximately monochromatic light. In this circuit the photocurrents in the two branches are

$$i_1 = kTI \text{ and } i_2 = kI$$

where  $k$  is a constant. The net current through the galvanometer is

$$i_0 = i_2 - i_1 = kI(1 - T) = kIA \quad (3)$$

where  $A$  is the absorption.

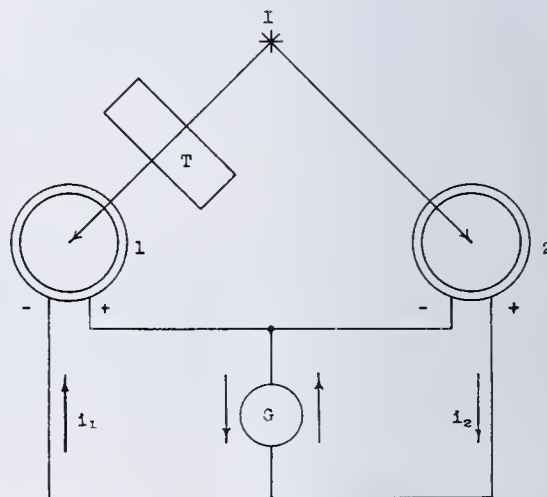


FIGURE 22. SIMPLE BALANCED CIRCUIT FOR BARRIER-LAYER CELLS

With a constant source the galvanometer will indicate the absorption directly. If the galvanometer sensitivity is adjusted by means of appropriate shunts it may be set to read full scale (100 divisions) when  $T = 0$ —i. e., when no light strikes cell 1. Under these conditions the scale will indicate per cent absorption. We may seek the condition for compensation for source fluctuations by differentiating Equation 3

$$di_0 = k dI - k T dI$$

Setting

$$\frac{di_0}{dI} = 0$$

we find that  $kTI = kI$  or  $T = 1$ .

In other words, fluctuations in response will be a minimum when the transmission of the sample is unity and the circuit has the doubtful distinction of perfect compensation when it is not in use. However, if optical compensation is used the compensating feature can be retained.

Circuit 2 (Figure 23). In this arrangement the two photocurrents,  $i_1$  and  $i_2$ , flow through variable resistors  $R_1$  and  $R_2$ .



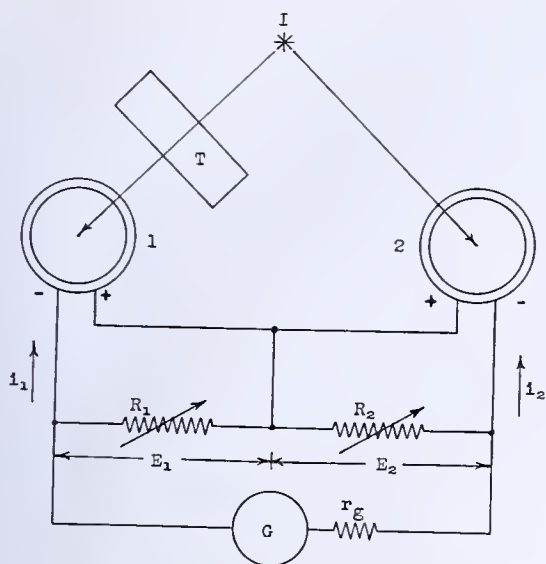


FIGURE 23. BALANCED CIRCUIT POSSESSING COMPENSATION FOR SOURCE FLUCTUATIONS

Values for the latter may be found such that the potential drops,  $E_1$  and  $E_2$ , are equal, under which circumstances the galvanometer will show zero deflection. The circuit was suggested by Wilcox (227). No circuit analysis was given and the following treatment which has been confirmed by experiment may be of interest.

As before

$$\begin{aligned} i_1 &= kTI & \text{and } E_1 &= kTIR_1 \\ i_2 &= kI & \text{and } E_2 &= kIR_2 \end{aligned}$$

at balance  $E_1 = E_2$  and therefore  $kTIR_1 = kIR_2$  or

$$T = \frac{R_2}{R_1}$$

The transmission of the sample is given by the ratio of the resistor settings necessary to establish balance. Various convenient arrangements are possible—for example,  $R_2$  may be a Kohlrausch slide wire and  $R_1$  an ordinary resistor of the radio “potentiometer” type. The slide wire is set at 100 with the sample removed and balance is established with  $R_1$ . The sample is then introduced and balance is re-established with the slide wire. The per cent transmission is indicated directly on the slide wire. Both resistors should have very low values for the reasons before-mentioned.

Compensation for source variations is inherent in this circuit. The current through the galvanometer is

$$i_g = \frac{E_2 - E_1}{rg} = \frac{kIR_2 - kTIR_1}{rg} \quad (4)$$

Differentiating

$$\frac{di_g}{dI} = \frac{kR_2}{rg} - \frac{kTR_1}{rg}$$

For

$$\frac{di_g}{dI} = 0$$

we get

$$T = \frac{R_2}{R_1}$$

From this result we see that the fluctuations due to source variations will be at a minimum when the resistors are set in the ratio of the transmission, which is precisely what is done in the process of balancing the circuit. This may be confirmed experimentally in simple fashion. Writing Equation 4 in increment form,

$$\Delta i_g = \frac{k \Delta I}{rg} (R_2 - TR_1) = \frac{k \Delta I R_1}{rg} \times \left( \frac{R_2}{R_1} - T \right)$$

since  $R_2/R_1$  is the transmission, any value of  $R_2/R_1$  may be designated as a virtual transmission,  $T'$ . The last equation becomes:

$$\frac{\Delta i_g}{\Delta I} = \frac{kR_1}{rg} (T' - T) = a \Delta T$$

where

$$a = \frac{kR_1}{rg}$$

Figure 24 shows values obtained and plotted according to the above equation. In this test  $R_1$  was held constant and the intensity of the common source was changed by known amounts,  $\Delta I$ . The corresponding galvanometer deflections,  $\Delta i_g$ , were noted. Several values of  $\Delta i_g/\Delta I$  were measured for different settings of  $R_2$ . In each case  $\Delta T$  could be computed from the value of  $R_2/R_1 - T$ . These are the abscissas of Figure 24, which shows that the fluctuations approach zero as the difference between  $R_2/R_1$  and  $T$  (the true transmission) approaches zero.

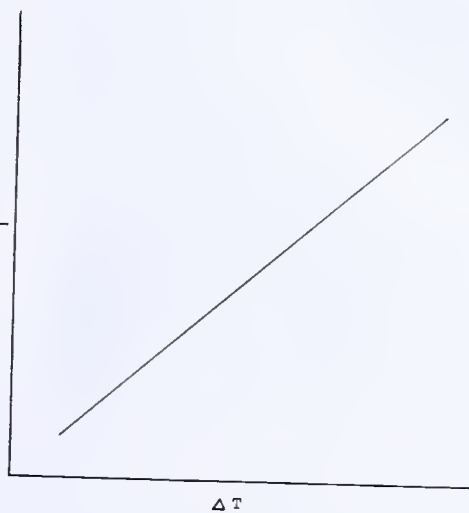


FIGURE 24

The limiting case is most simply shown by setting  $R_2/R_1$  equal to the true transmission. The light source may now be dimmed almost to extinction without causing any perceptible galvanometer deflection.

Circuit 3 (Figure 25). This arrangement with various modifications has been widely employed. Brice (19) has given an analysis of this and related circuits. Neglecting secondary factors, this method may be used to obtain transmission values with good compensation

for source variations. Figure 25 shows that the galvanometer may be considered as fed by two cells through universal shunts. In the right-hand branch,  $R$  may take the form of a low-resistance Kohlrausch slide wire.

The opposing currents through the galvanometer may be written

$$i_{g1} = kTI \frac{a}{R + rg}$$

$$i_{g2} = kI \frac{x}{R + rg}$$

At balance these currents are equal; hence

$$x = Ta$$

In other words,  $x$ , the slide-wire setting, is directly proportional to the transmittancy; indeed, if the initial adjustment is so arranged that when  $T = 1.00$ ,  $x$  is set at its maximum value,

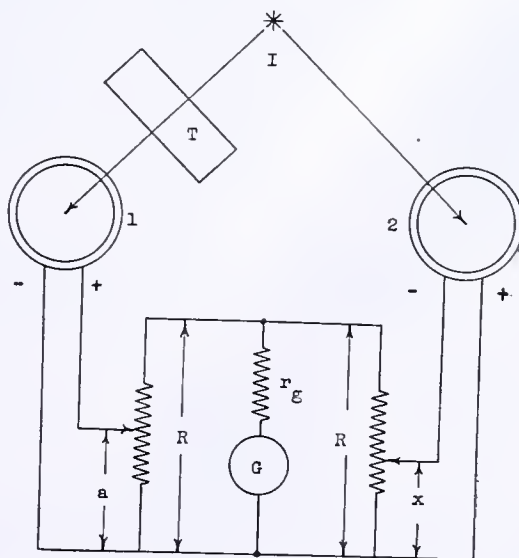


FIGURE 25. BALANCED CIRCUIT  
Direct reading, with compensation for source fluctuations







extent all such calibrations are burdened with an instrumental constant or factor. It is only when all photoelectric photometers employ strictly monochromatic light that a table of appropriate extinction coefficients will be of general value and will eliminate the necessity of individual calibration.

5. INTERPRETATION OF RESULTS. Reliable photometric measurements of this sort will provide immediate information concerning the validity of Beer's law. Despite the many contradictions in the literature, very careful and precise measurements have indicated that it is usually applicable, including colloidal dispersions, provided there is no appreciable change in particle size. There are obvious cases, such as concentrated cupric salts, in which very profound changes in color are associated with dilution and in such instances pronounced deviations from Beer's law are to be expected. With the exception of such obvious cases, in which many physical properties of the system would lead one to expect deviations, the existence of a definite extinction coefficient at a given wave length is to be regarded as a fundamental physical property of the system. The failure of Beer's law should not be claimed unless the experimental method is known to be beyond reproach.

This criterion of colorimetric reactions will become increasingly important as photometric practice becomes more precise and reliable. At the present time our fund of color reactions is very large, although, unfortunately, very few have been investigated rigorously enough to satisfy the above criteria. Indeed it may be said that we have far too many methods; that few will survive critical examination. It is not the object of this review to discuss these reactions in detail nor even to question the expediency of certain proposed tests, but rather to emphasize the need for rigorous optical and physico-chemical examination of each reaction. As a rule the purely analytical aspects such as selectivity, interference, etc., have been adequately investigated.

### Photometric Titrations

The type of measurement just discussed places a heavy burden of responsibility upon a single photometric measurement. Ordinary volumetric analysis permits high precision because a relatively large volume of reagent can be measured to within one drop. The actual color change at the end point is rarely estimated (in the optical sense) to better than 5 or 10 per cent, yet this change is sufficiently abrupt to afford sufficient precision. Photoelectric methods have been used to detect such changes (16, 76, 96, 140, 142, 173, 193, 194); indeed, titrations can be performed automatically (149) when a large number of routine analyses warrant the necessary elaboration in equipment. In a larger sense, however, photometric titrations may supplement or replace the ordinary photometric procedure. The well-known "duplication method" of colorimetry involves the treatment of the unknown with a large excess of reagent. In a comparison vessel filled with excess reagent, a standard solution of the substance is added in amount sufficient to match the color of the unknown sample. The conditions necessary for the success of this method are completely discussed in standard texts and will not be repeated here (105).

For those systems in which it is applicable, the photoelectric method may be used in a number of ways—for example, a sensitive twin-cell photometer may be used to indicate the point at which the two solutions have identical transmissions. A more laborious but very precise procedure involves a measurement of the transmission at uniform intervals during the titration. If Beer's law is obeyed, a plot of  $-\log T$  (extinction) will be a linear function of the amount of reagent. Moreover, if the color reaction follows a definite stoichiometric law a sharp inflection may be expected in the extinction lines when reagent and substance react in equivalent amount. The technique is reminiscent of conductance titrations; indeed, the average straight lines may be considerably more reliable than the individual points.

The latter method is useful in clearing up certain points of theoretical interest. By this method it has been shown (148) that the gold method for estimating bromides really involves the  $\text{AuBr}_4^-$  ion as the light-absorbing species, not a wholly unexpected result, but more convincing than indirect reasoning or supposition. Similarly, certain peculiarities of the starch-iodine system have been studied in this manner (147).

It is likely that studies of this sort would be profitable in the case of most colored substances in solution. In too many cases the composition of the colored substance has been inferred from the nature of the solid phase which can be obtained from the solution, or as one often suspects, from the ease with which an equation may be balanced in an elementary textbook. A classic example is the familiar reaction between ferric and thiocyanate ions (190, p. 284).

It is not unlikely that the results obtainable by the technique of photoelectric titrations would warrant the design and construction of a recording photometer.

### Automatic Inspection and Control

Modern trends in industry show increasing use of automatic measurement and control. Many operations are in reality chemical analyses, but the operator has been dispensed with and self-regulated, self-calibrated instruments take over the burden. Of the various properties of a system which lend themselves to analytical purposes, one may mention density, viscosity, conductance, dielectric constant, etc. No one property is superior; there is hardly ever a "best method," but the choice of the determining property and the means of measuring it are governed by the circumstances. The cases which will be mentioned are those which solved the problem satisfactorily even though alternative schemes might have been used. Photoelectric methods have been used for the obvious chore of counting objects, classifying, and grading according to size, color, or temperature (incandescence) (*F, I, K, N, Q, R, U*). Distinctly optical criteria of a system naturally lend themselves to photoelectric methods—for example, turbidity, color, gloss, refractive index, optical activity, and opacity (smoke).

The conventional methods of colorimetric analysis have been reduced to automatic practice, usually by the expedient of by-passing (bleeding) a portion of the system, sampling, then injecting an appropriate reagent, after which the mixture is photometered. The measurement in this case may be in absolute terms or relative to an arbitrary standard. Usually a conventional electrical recorder (recording potentiometer or Wheatstone bridge) provides a permanent record. For control it is fitted with limit relays which initiate appropriate corrective measures (addition of acid or alkali, change of temperature or pressure, etc.). Such installations are further complicated by the need for auxiliary equipment, as, for example, periodic self-calibration, antihunting mechanisms, or circuits to prevent overcompensation. Unless elaborate precautions of this sort are provided by intelligent engineering design, the instrument or controller is likely to act like an unruly monster. The fundamental idea behind most photoelectric controls is relatively simple, but reference to typical installations (*K*, p. 230; *2*, 53) shows the expenditure of great ingenuity and care in the realization of the scheme from an engineering point of view.

### Applications

While it is obvious that any suitable colorimetric reaction may be treated by appropriate photoelectric means, it may be helpful to record some instances of actual problems which have been solved by the use of photoelectric cells. Further



possibilities are to be gleaned from standard treatises on colorimetry (190, 233). Photoelectric instruments have been used in the analysis or measurement of water (3, 17, 113, 172, 187, 218, 221), gas (21, 22, 74, 120, 191), foods (151, 230), steel (9, 194), textiles (4, 20, 179, 185, 189), leather (12), titrations (16, 76, 96, 140, 173, 193, 194), combustion (170), colloids (181), serum (155), oils (13, 123, 127, 178, 202, 203), beer (35, 110, 199), fertilizers (135), sugar (83, 177, 196), chlorophyll (73, 188), pH (122, 124, 125, 143, 150), reaction kinetics (18, 79, 98, 138, 176), dust (100), indicators (125, 182), dyes (94, 157), clinical (25, 37, 38, 45, 46, 101, 103, 121, 168, 175), sedimentation (136), turbidity (26, 64, 76, 95, 97, 99, 102, 126, 150, 198), carbon dioxide (22), hydrogen sulfide (21), alkalies (93), alkaline earths (93), and bacteria (7).

### Conclusions

The current literature indicates a widespread and increasing interest in photoelectric methods. Measurements have been reported which exceed in precision and reliability the values which can be obtained with the very best visual instruments (85, 107, 125, 128, 129, 130, 133, 158, 159, 238). These results are invariably obtained with instruments which embody sound optical theory and practice and the best resources of electrical measurements. They are usually photoelectric spectrophotometers, and are necessarily elaborate and expensive. Simple compromise instruments have been described in great number and are justified by reasons of expediency, elimination of fatigue, or greater speed of operation. They rarely justify exaggerated claims of superiority over existing visual instruments.

Photoelectric cells are available in great variety and at low cost. Circuit adjuncts such as improved meters, vacuum tubes, thyatron, and indicator tubes are increasingly available and in many cases have been designed specifically for use with photocells. Countless circuit possibilities have been published in various papers and monographs, but a very small fraction of these have been applied to chemical problems.

Applications have been directed for the most part to analysis, and therefore have served as an improved adjunct to the highly developed field of colorimetric analysis. In addition they have served a useful purpose in pH measurements, kinetics, and the study of the composition of colored solutes.

The increasing number of problems and the complexity and diversity of modern devices seem to imply that future research will require greater cooperation between the chemist and the radio engineer or that each shall become more fully acquainted with the problems and resources of the other field. Specifically, the engineer is unaware of the nature and needs of the chemist's problems. Similarly, the chemist is, in most cases, unfamiliar with the possibilities of electronic circuits and how they may be modified to suit his purpose. One is constantly surprised by the spirit of "rediscovery" which seems to pervade the chemical literature dealing with photoelectric photometry. For this reason, the writer has listed in the bibliography a separate group of monographs. Repeated reference is made in the body of this paper to these sources; indeed, the review can be considered as little more than a summary of the advice and good counsel which is to be found in these sources.

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# The Action of Ethanolamine on Woody Tissue

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IN 1937 Van Beckum and Ritter (8) published a revised technique for the determination of holocellulose, which represents very nearly the total carbohydrate fraction of the cell wall, as well as part of the methoxyl and the larger share of the acetyl groups present in the original wood. In their modification, these investigators used alternate treatments with chlorine and 95 per cent ethyl alcohol containing 3 per cent of monoethanolamine. In August, 1935, the first experiments with pure anhydrous ethanolamine and dry wood were carried out at Syracuse.

In the authors' first experiments oven-dried wood samples [large-tooth aspen (nomenclature of species according to 7), which had been subjected to complete analysis by Richard D. Freeman] were extracted with monoethanolamine, just below the boiling point of the solvent (about 168° C.) for 5.25 hours. One hundred cubic centimeters of the base were used for about 3 grams of wood. At the end of the extraction the material was filtered by suction and washed with water until the filtrates were colorless. The brown residue was dried to constant weight. A lignin determination (made by the cold sulfuric acid method of the U. S. Forest Products Laboratory, 6) showed that 2.62 per cent of lignin remained in the pulp. Based on the original dry wood, this corresponded to 1.73 per cent of lignin.

A summative analysis thus showed the following:

Total loss of wood on extraction with ethanolamine	33.80
Residual lignin	1.73
Cross and Bevan cellulose (determined by R. D. Freeman)	64.42
Total	99.95

A very similar result was obtained by the ethanolamine extraction of spruce wood.

In another experiment (with a view towards complete delignification) 1 gram of oven-dried beech heartwood sawdust was extracted for 5 hours with 50 cc. of ethanolamine in an oil bath kept at approximately 170° C., so that the solvent in contact with the wood was just below the boiling point. Heating could be carried out satisfactorily in an Erlenmeyer flask, fitted with a funnel, covered with a watch glass. Cork or rubber stoppers were avoided.

The mixture was diluted with 50 cc. of water and the residue collected on a fritted-glass crucible, washed with water, and then bleached for 20 minutes with water saturated with chlorine, in a covered beaker but without removing the cellulose residue from the crucible at any time. The contents of the crucible were sucked dry, and the crucible was then filled with a solution of sulfurous acid. After standing 3 minutes this was removed by suction, and the residue washed with water. Crucible and residue were then placed in hot aqueous 3 per cent sodium sulfite solution for 0.5 hour, during which time a faint pink color developed. Although the residue after washing was white, chlorine water, water, sulfurous acid solution, and water successively were again passed through the crucible to assure a final bleach. The residue was thoroughly washed with water containing a trace of ammonia, and the crucible and residue were dried to constant weight.

The following results were obtained:

Ethanolamine cellulose	60.4, 60.5
Cross and Bevan cellulose on the same sample, determined by R. D. Freeman (av. of 3 determinations)	60.7

Although the analytical procedure by the ethanolamine method given for beechwood should be checked with a large number of woods, it seems probable that it will yield a residue comparable to Cross and Bevan cellulose. If so, it has much to recommend it over the procedure for isolating the latter. No preliminary extractions are required, and the manipulations are much simpler.

More recently Harlow and Wise (2), determining cellulose in the woody portions of rhizomes of brake fern, obtained

29.4 per cent of cellulose (by the Cross and Bevan method), and 30.0 per cent of cellulose (by extraction with pure ethanolamine, followed by mild successive treatments with hydrochloric acid, chlorine water, water, sulfurous acid, and water).

Evidently this anhydrous ethanolamine delignification gives a residue corresponding very closely to Cross and Bevan cellulose, and removes from the wood not only most of the lignin, but also a large amount of the "cellulosan" fraction and extraneous materials.

In 1925 Ritter (5) chlorinated thin sections of wood and observed the treated sections with a microscope. Delignification resulted in a separation of the cells, presumably by the dissolution of the middle lamella. Similar experiments were subsequently made by one of the authors (1) and it was further noted that the lignin in the secondary walls could be removed by mild chlorination before appreciably attacking that in the middle lamella, as shown by the effect of 72 per cent sulfuric acid on such treated material. The substance (presumably a precursor of coniferyl aldehyde, 3) responsible for the phloroglucinol color test for "lignin" was also removed upon mild chlorination of thin wood sections.

## Visual Effect of Monoethanolamine

To determine the visual effect, shown by the microscope, of monoethanolamine on thin (10 $\mu$ ) transverse sections of woody tissue (cut from blocks of dry sapwood, previously aspirated under cold water, and stored in 15 per cent ethyl alcohol), sections of red pine, sitka spruce, red alder, and catalpa were allowed to stand in the cold reagent (15° C.) for a number of weeks and examined periodically for possible evidences of delignification.

After 3 days portions of the sections were removed, washed in water, and treated with phloroglucinol reagent and 72 per cent sulfuric acid, respectively. In the first instance the typical scarlet color obtained on untreated material was not seen but rather an orange-red appeared. Treatment with the acid did not produce any visible disintegration of walls resistant in untreated sections.

After 2 weeks in cold ethanolamine the characteristic red color with phloroglucinol failed to develop, and all sections were yellowish. At this point the secondary walls of the two conifers, and the vessel walls in red alder, showed signs of partial disintegration when immersed in acid. At the end of 3.5 months' treatment with ethanolamine, the secondary walls disintegrated almost completely when subjected to 72 per cent sulfuric acid. In all cases a middle lamella network (Kerr and Bailey's "compound middle lamella," 4) remained, indicating that the cold reagent, although able to remove the secondary cell-wall lignin, did not appreciably attack that of the central layers. Wood sections of cottonwood, white fir, tupelo, chestnut, red spruce, eastern red cedar, and lodgepole pine were treated for 10 days at 28° C. and results similar to those noted above (at 15° C.) were obtained.

Experiments with boiling ethanolamine on sections of red pine, sitka and red spruces, southern white cedar, Deodar cedar (*Cedrus deodar*), bigtree, eastern white pine, western hemlock, and Douglas fir, gave results comparable to those at lower temperatures, except that delignification was accomplished in a fraction of the time necessary in the cold, and further, the true middle lamella or intercellular substance was attacked and almost, if not entirely, removed. Usually



from 2 to 6 hours were necessary to delignify sections to the point where the cells barely adhered to each other, and were completely soluble in 72 per cent sulfuric acid.

In all cases the visual effect of boiling monoethanolamine on wood sections seemed the same as that obtained by subjecting them to chlorination, or bromination followed by hot dilute sodium sulfite, or 10 per cent ammonium hydroxide. These results appear to reinforce the analytical data which indicate that the amounts of "ethanolamine cellulose" and Cross and Bevan cellulose isolated from a given sample are approximately the same.

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# Determining Organic Carbon in Soils

## A Modification of the Chromic Acid Reduction Method

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THE current popularity of rapid chemical tests as a means for estimating the crop-producing power of a soil makes desirable a rapid method for determining the organic carbon content of the soil. The chromic acid reduction method as proposed by Schollenberger (3, 4), with its various modifications, is being widely used for this purpose. Constant and reproducible results may be obtained with this method, as has been shown by Degtjareff (2) and by Allison (1). Although Allison found that the method recovered but 86.9 per cent of the carbon present when compared to the standard furnace combustion method, this percentage recovery was so near constant for the sixty-six soils studied that by use of a factor (carbon found by chromic acid reduction multiplied by 1.15) he obtained almost identical results with the two methods.

Although considerably faster than furnace combustion, the Schollenberger method still consumes considerable time when a number of determinations are made. A modification which would eliminate the necessity of heating each determination separately, without impairing accuracy, would greatly reduce the time factor and would prove of considerable value in those laboratories where a large number of determinations of soil organic matter are made in routine analysis. Various modifications have been suggested, but in these changes the accuracy of the method is usually sacrificed. This paper presents data obtained in an attempt to overcome this difficulty, and describes a procedure that has given results in close agreement with those obtained by the original Schollenberger method.

Briefly stated, the chromic acid reduction method consists of oxidizing the organic carbon in a small sample of soil (0.2 to 0.5 gram) with a measured quantity of standardized chromic acid in sulfuric acid, and determining the extent of reduction of the chromic acid by titration with 0.2 N ferrous ammonium sulfate, using diphenylamine as the indicator.

Walkley and Black (5) proposed that the oxidation of the organic matter be induced by the heat of reaction between sulfuric acid and water, but claimed a recovery of only 60 to 86 per cent of the carbon present. Allison (1) found the maximum temperature obtained in this reaction to approximate 124° C. and stated that this is insufficient to recover a definite fraction of the organic carbon present in different soils.

Degtjareff (2) proposed two modifications. In one he brought about the oxidation of the organic carbon by the addition of a mixture of chromic acid and hydrogen peroxide to the soil sample. Walkley and Black (5) showed that this method gives entirely fictitious results, since the hydrogen peroxide reacts differently

with chromic acid in the presence of soil than in the corresponding blank. Degtjareff's other proposal consisted in oxidizing the organic matter by heating the acid-soil mixture for 10 minutes at 165° C. in a sulfuric acid bath. He stated that the chromic acid oxidizing solution, prepared by heating for one-half hour at 165° C., shows no change in titer when run according to the above procedure. This would seem to conflict with Schollenberger's inference of the importance of temperature-time relationship upon the stability of the chromic acid oxidizing solution. Schollenberger specified that the acid-soil mixture be heated to 175° C. in approximately 90 seconds over an open flame. Tests show that even this brief heating reduces the titer of the 10-ml. aliquot of a 0.408 N chromic acid solution to 0.396 N, the loss being due to evaporation and reduction of the chromic acid in direct contact with the glass container which may reach a temperature of 800° C. when heated by an open flame.

To test Degtjareff's proposal, 10-ml. portions of chromic acid solution were placed in 25 by 150 mm. test tubes and heated for 10 minutes in a sulfuric acid bath at various temperatures. The results obtained are presented in Table I.

TABLE I. TEST OF DEGTJAREFF'S METHOD

Temperature of H <sub>2</sub> SO <sub>4</sub> Bath ° C.	Normality of Chromic Acid	Loss in Normality
100	0.408	0.000
120	0.408	0.000
140	0.400	0.008
160	0.382	0.026
180	0.336	0.072

Although a number of samples could be oxidized at once by this method, the accuracy of the procedure is greatly impaired. The partially reduced chromic acid solution in the tube containing soil would naturally lose less in titer than would the stronger solution in the blank determination. In a determination where the normality of the blank chromic acid solution was reduced 0.026, a soil was found to contain 2.10 per cent of organic carbon. The same soil showed only 1.74 per cent of organic carbon when higher heating reduced the normality of the blank by 0.072.

It would seem that the accuracy of the method depends upon bringing about a rapid oxidation of the organic matter by heating to a temperature sufficiently high to ensure complete oxidation in as short a time as possible in order to prevent loss of titer in the 10-ml. aliquot of the chromic acid solution due to evaporation and reduction. As an electric oven seemed to offer a means of accomplishing this purpose, the oven shown in Figures 1 and 2 was constructed.



A metal trough,  $12.5 \times 11.25 \times 30$  cm. ( $5 \times 4.5 \times 12$  inches), was made of Cop-r-loy. The ends, sides, and bottom of this trough were lined with two thicknesses of 0.8-cm. (0.3-inch) asbestos board which was held in place by refractory cement. Next 16 meters (52 feet) of No. 24 Chromel C wire were coiled and fastened to one side of a false bottom of asbestos board cut to fit snugly in the bottom of the box. The wire was then tapped as shown in Figure 2, the completed heating unit drawing approximately 1,440 watts when operated on a 120-volt current.

For the top of the oven, two pieces of asbestos board were cemented together, and ten 2.66-cm. (1.06-inch) holes were drilled through the top in two tiers, providing a close fit for test tubes 25 mm. in diameter. To prevent the test tubes from resting directly on the heating unit, a strip of 0.6-cm. (0.25-inch) mesh screen wire was placed approximately 3.75 cm. (1.5 inches) above the heating unit in the oven. This permitted only 3.1 cm. (1.25 inches) of the test tube to be exposed to the direct heat of the oven, thereby reducing the heated surface of the glass and the loss by evaporation.

TABLE II. TEST OF OVEN HEATING

Soil Type	Organic Carbon Heated to 175° C. in open flame in 90 seconds	Organic Carbon Heated to 175° C. in oven in 3 minutes
	%	%
Sassafras sandy loam	0.65	0.64
Norfolk fine sandy loam	0.80	0.80
Elkton sandy loam	2.33	2.36
Keyport sandy loam	2.58	2.61
Dismal swamp peat	5.22	5.28

The completed oven is capable of an operating temperature of approximately 400° C., and this temperature is sufficient to raise that of 10 ml. of chromic acid solution inserted in a 25 by 150 mm. test tube to 175° C. in approximately 3 minutes. Furthermore, the normality of the chromic acid solution is reduced by only 0.008, just two-thirds the reduction brought about by heating to 175° C. in 90 seconds over an open flame. This lower loss in titer is explained by the lower maximum heat of the oven (400° C.) when compared to that of an open flame (approximately 800° C.), and by the fact that only the lower third of the test tube is heated, the balance of the tube acting as a condenser.

To test oven heating with open-flame heating, five soils varying in organic matter content were chosen. The results, presented in Table II, show that oven heating is quite as satisfactory as heating over an open flame. Ten samples may be oxidized in 3 minutes, the tubes removed from the oven, placed in cold water to be titrated later, and ten fresh tubes inserted in the oven. One hundred samples may be

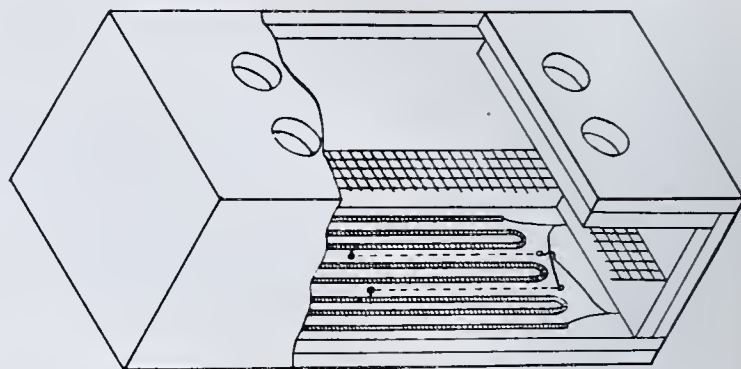


FIGURE 2. DIAGRAM OF OVEN

oxidized within an hour with a greater uniformity of heating than is possible where an open flame is used.

In the course of the foregoing investigation another minor modification, dealing with the preparation of the chromic acid oxidizing solution, was made in Schollenberger's procedure. It is recommended that this solution be prepared as follows:

Place 10 grams of powdered potassium dichromate, previously oven-dried at 100° C. for one hour, and 500 ml. of a 1 to 1 mixture of phosphoric and sulfuric acids in a 1-liter flask. Then heat the flask in a boiling water bath for 1 hour, occasionally stirring the mixture. Solution of the salt will be complete and the titer of the solution will remain constant, closely approximating 0.4 *N* in oxidizing power. The advantage of this modification is twofold. It eliminates the necessity of later adding phosphoric acid to activate the diphenylamine indicator during the titration with ferrous ammonium sulfate, and by changing the ratio of phosphoric to sulfuric acid from 1 to 2, to 1 to 1, a much sharper end point for the titration is obtained. The substitution of the phosphoric acid for half the sulfuric acid in the oxidizing solution in no way affects the strength of this solution.

### Summary

An investigation of the temperature-time relationship in the determination of the organic carbon of the soil by the chromic acid reduction method is reported. A laboratory-constructed electric oven which provides a uniform method of oxidizing ten samples in 3 minutes is described, along with a modification in the preparation of the chromic acid solution which saves time and increases the sharpness of the end point during the titration with ferrous ammonium sulfate.

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RECEIVED September 19, 1938.

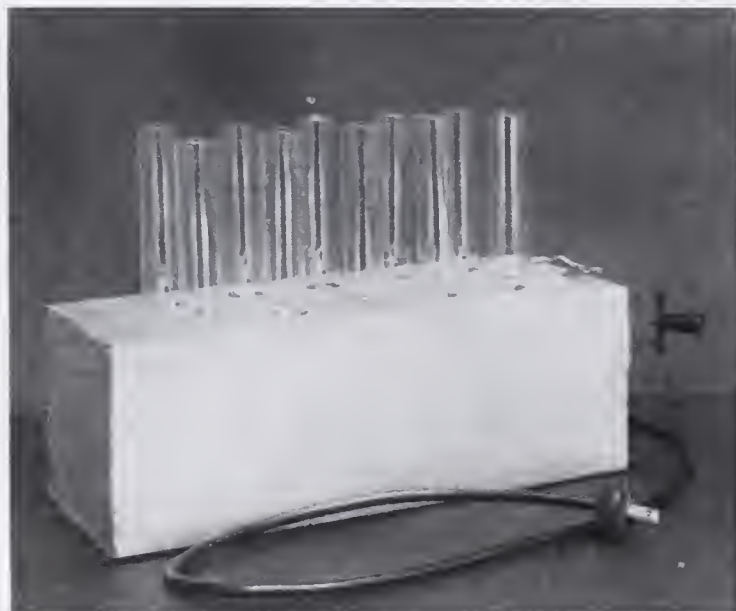


FIGURE 1. OVEN

## Prevention of Sticking of Buret Stopcocks

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AFTER considerable trouble with burets used for sodium hydroxide solution, sodium thiosulfate solution, and other reagents, it was found that the sticking of buret stopcocks, when not in use, may be prevented by simply keeping the lower part of the buret containing the stopcock immersed in a beaker of distilled water.

RECEIVED December 2, 1938.



# Determination of Fluorine

## With Special Reference to Analysis of Natural Phosphates and Phosphatic Fertilizers

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**T**HE determination of fluorine in most materials requires its separation from other constituents of the sample. For this separation volatilization (or distillation) methods, being relatively rapid, have been favored whenever the fluorine-bearing constituents were readily soluble in acid, whereas fusion with alkali compounds with subsequent separation of the fluorine by rather cumbersome precipitation methods has been the rule with acid-insoluble materials. The chief carrier of fluorine in natural phosphates is apatite (12), and calcium fluoride has been identified in a few instances as a constituent of phosphate rock. Fortunately, both compounds can be treated successfully by distillation methods. On the other hand, fusion with alkali fluxes is not very effective in decomposing apatite (22).

The volatilization method (25, 27) used prior to about 5 years ago was not entirely satisfactory. One of the principal difficulties arose from the interfering effect of gelatinous silica, which renders the method inapplicable to materials that contain acid-decomposable silicates (23). Furthermore, the method of Reynolds and Jacob (22), involving fusion and acid extraction of the sample with subsequent precipitation of the fluorine as lead chlorofluoride, was very tedious and gave low results on some types of phosphate rock, such as Tennessee blue rock and Florida waste-pond phosphates.

The publication of a volumetric method by Willard and Winter (28) in 1933 marks a great forward step in the analysis of fluorine-containing materials. In simplicity of requisite apparatus, ease of manipulation, speed, and quality of results, this is far superior to any other known method for the analysis of a wide variety of materials.

In the original procedure fluorine is (1) separated from the sample (fused with alkali carbonate if the fluorine compounds are not decomposed by acid) by distillation with sulfuric acid or perchloric acid and (2) determined in the neutralized distillate, after the addition of an equal volume of ethyl alcohol, by titration with standard thorium nitrate with the use of zirconium-alizarin indicator. Armstrong (2) omitted the

zirconium salt from the indicator used for titrating very small amounts of fluorine. Because of the greater sensitivity of the simplified indicator to changes in the pH of the solution during titration, it was not satisfactory for the titration of several milligrams of fluorine in a slightly buffered solution (20), such as was used at that time. Later, the advent of the use of a buffer solution (16) to control the pH during titration made the addition of a zirconium salt to the indicator unnecessary for the titration of the larger quantities of fluorine. The almost constant attention required to maintain the temperature of distillation within the permissible range by the frequent additions of small quantities of water to the distilling flask was overcome by means of a form of steam distillation (24).

With the foregoing improvements the Willard and Winter method has been used in this laboratory on a wide variety of natural phosphates and phosphatic products. A number of observed interfering factors have been investigated from time to time—for example, the effect of neutral salts on the titration, and the uncertainty of the results obtained on pyritiferous samples. The results of these studies are presented in this paper.

### Preparation of Pure Sodium Fluoride

Hoffman and Lundell (14) prepared a sodium fluoride of high purity from sodium bicarbonate and redistilled hydrofluoric acid by a modification of the method used by McAdam and Smith (19) in their atomic weight work. The authors prepared a very good grade of sodium fluoride from reagents meeting A. C. S. specifications as follows:

Evaporate 100 grams of 48 per cent hydrofluoric acid in a platinum dish to about two-thirds of its volume. Heat 20 grams of sodium bicarbonate and 75 ml. of distilled water in a platinum dish until the salt dissolves. Filter with the aid of a hard-rubber funnel, and to the clear solution add slowly with constant stirring (platinum rod) the entire amount of prepared acid. Heat the acid solution carefully until the carbon dioxide is expelled and the solution becomes clear, then evaporate it to dryness, and gradually increase the temperature to 350° to 400° C. If a

Several factors that cause interference in the determination of fluorine were studied by distilling the sample with perchloric, phosphoric, or sulfuric acid and titrating the distilled fluorine with thorium solution.

The titration is markedly affected by orthophosphate, sulfate, and hypochlorite ions and to a much less extent by alkali, borate, and sulfide ions. In the concentration range studied arsenite, chlorate, and silicate ions have no observable effect. Interference is greatly reduced and a sharper end point is obtained when the titration medium is an aqueous instead of an alcoholic solution.

Difficulties arise from substances, such as (1) aluminum compounds and gelatinous silica, that retard the distillation of fluorine, and (2) the distilling acid, phosphate, pyritic sulfur, organic materials, and halogens other than fluorine, that are incompletely separated from the fluorine and cause trouble in the subsequent titration. When perchloric acid is used as the distilling acid, the distillates of most types of phosphate rocks studied carry negligible quantities of perchlorate and phosphate. The separation of fluorine from pyritic sulfur and organic matter is improved by distilling the sample in the presence of an excess of permanganate.



flame is used, provision should be made to protect the salt from contact with combustion gases. Continue the gentle ignition under the hood until the escape of hydrofluoric acid ceases, and finally ignite the product to constant weight in a muffle furnace at 650° C. Theoretical yield, 10 grams.

As shown volumetrically by comparing its thorium nitrate titer with that of a sodium fluoride of known purity (prepared and carefully analyzed several years ago by C. M. Smith of the Division of Insecticide Investigations, Bureau of Entomology and Plant Quarantine), and also gravimetrically by conversion to sodium sulfate, the product prepared by the authors by the foregoing procedure was 99.7 per cent sodium fluoride.

### Titration of Alkali Fluoride with Thorium Nitrate Solution

Besides the titration medium and the presence of interfering substances, the factors that affect the titration of alkali fluoride with thorium nitrate include pH of the solution, concentration of the indicator, fluoride concentration, and temperature. In the work reported here, the pH of the solu-

tion was controlled with the aid of a buffer solution (prepared by neutralizing to phenolphthalein 200 ml. of 1 *M* monochloroacetic acid with alkali hydroxide, adding to the neutralized solution 200 ml. of the 1 *M* chloroacetic acid, and diluting to 1 liter), which with a few indicated exceptions was used at the rate of 0.5 ml. per 10 ml. of initial volume ( $V_i$ ) of the solution for titration. One drop of indicator solution (0.1 per cent solution of sodium alizarin sulfonate) was used for each 10 ml. of initial aqueous solution. With the amounts of fluorine involved in this work the observed effect of indicator concentration is about the same as that noted by Dahle *et al.* (5) in the titration of smaller quantities of fluorine. For example, in the titration of 3.8 mg. of fluorine in 50 ml. of aqueous solution the authors found that a 50 per cent decrease or increase in indicator concentration changed the titer +0.04 or -0.04 ml., respectively, of 0.04 *N* thorium nitrate. All titrations were made at room temperature (20° to 30° C.). An increase in temperature results in slightly lower titers.

**THE TITRATION MEDIUM.** Willard and Winter titrated in 50 per cent alcohol. Although Armstrong (1) showed that the alcohol can be omitted in the titration of up to 0.01 mg. of fluorine in buffered solution, only recently Rowley and Churchill (26) have proposed that the titration of larger quantities be conducted in aqueous solution. The omission of alcohol would be a desirable simplification.

In Figure 1 are shown several curves plotted from results obtained by titrating different quantities of sodium fluoride with thorium nitrate solution with and without the use of alcohol. In each case the curves are sensibly straight lines over the useful part of the range. Furthermore, the linear relationship holds for quantities of fluorine up to 50 mg. at least (results not shown). The blank titration is somewhat larger in aqueous than in alcoholic solutions, and for a given normality of thorium nitrate it increases with  $V_i$  (Figure 1, b). With moderately small quantities of fluorine the results for aqueous solutions depart from a straight line in the vicinity of 0.1 mg. of fluorine, whereas the results for alcoholic solutions do not (Figure 1, a). Aside from this behavior, which occurs near the lower limit of the range for 0.01 *N* thorium nitrate, aqueous solution is just as satisfactory as an alcoholic medium for the titration of pure solutions of sodium fluoride. The authors' experience, in general, confirms the observation of Rowley and Churchill (26) that a more distinct end point is obtained in aqueous solution; however, the sharpness of the end point is affected considerably by the initial volume, even though the concentration of the indicator be kept constant.

The observation of Lockwood (18) that a sharper end point is obtained in glycerol-water solution than in ethanol-water solution could not be confirmed by the authors.

**INTERFERING IONS.** Willard and Winter (28) state that "Any ion that forms a precipitate or a nondissociated salt with fluorine or thorium interferes with the titration—e. g.,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{PO}_4^{---}$ , etc." Hoskins and Ferris (16) give quantitative data on the permissible concentrations of a number of ions likely to be met in the distillates of natural materials. Their experiments, which were confined to negative ions (halogen,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_3^{--}$ ,  $\text{AsO}_3^{--}$ ,  $\text{SO}_4^{--}$ ,  $\text{AsO}_4^{--}$ , and  $\text{PO}_4^{--}$ ) in alcoholic solution, show that an appreciable effect appears when the halogen, nitrate, or perchlorate concentration reaches about 0.1 *M*, whereas the permissible concentration of the other ions is of the order of  $10^{-3}$  *M*, or less. Quantitative data on the effect of barium chloride and carbon dioxide have appeared recently (10). As far as the authors are aware no one has published data on the effect of alkali ions, or the interference of ions, with the exception of  $\text{Cl}^-$  and  $\text{ClO}_4^-$  (1, 9), when the titration is made in aqueous solution.

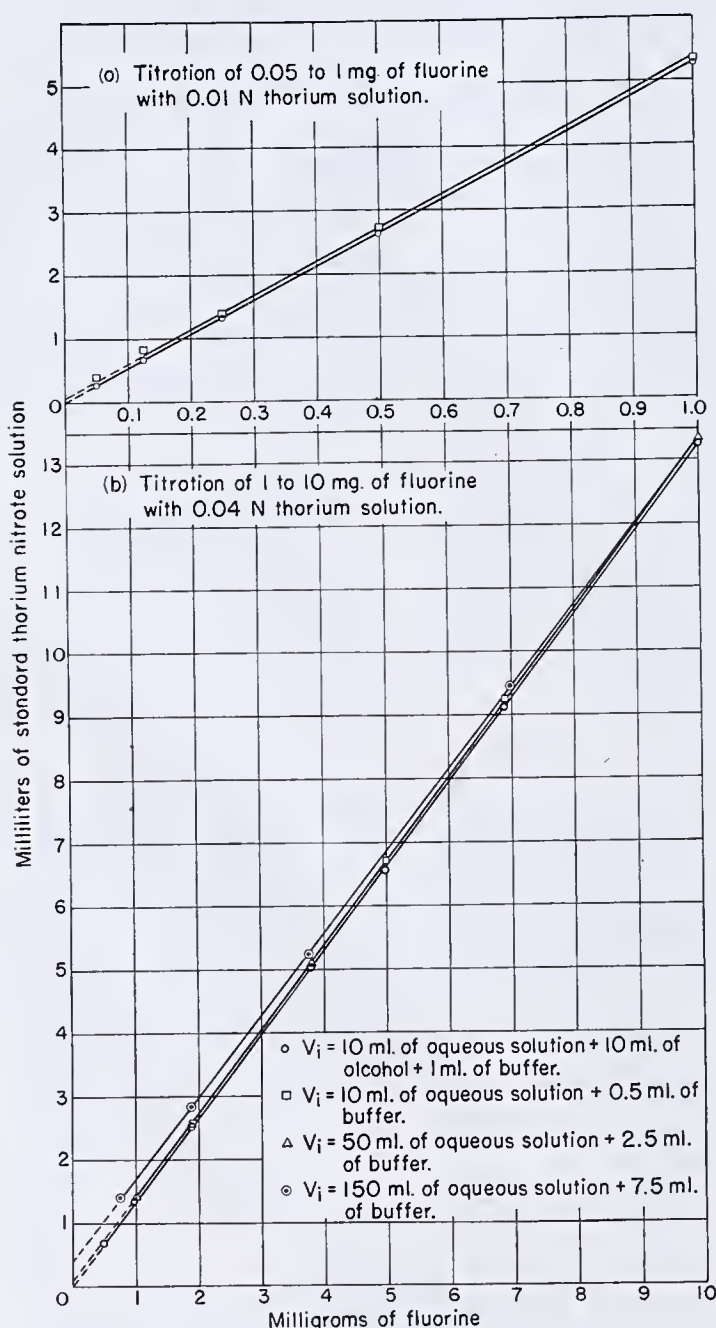


FIGURE 1. STANDARDIZATION OF THORIUM NITRATE SOLUTION AGAINST SODIUM FLUORIDE

By titration of 0.05 to 10 mg. of fluorine in aqueous and alcoholic solutions



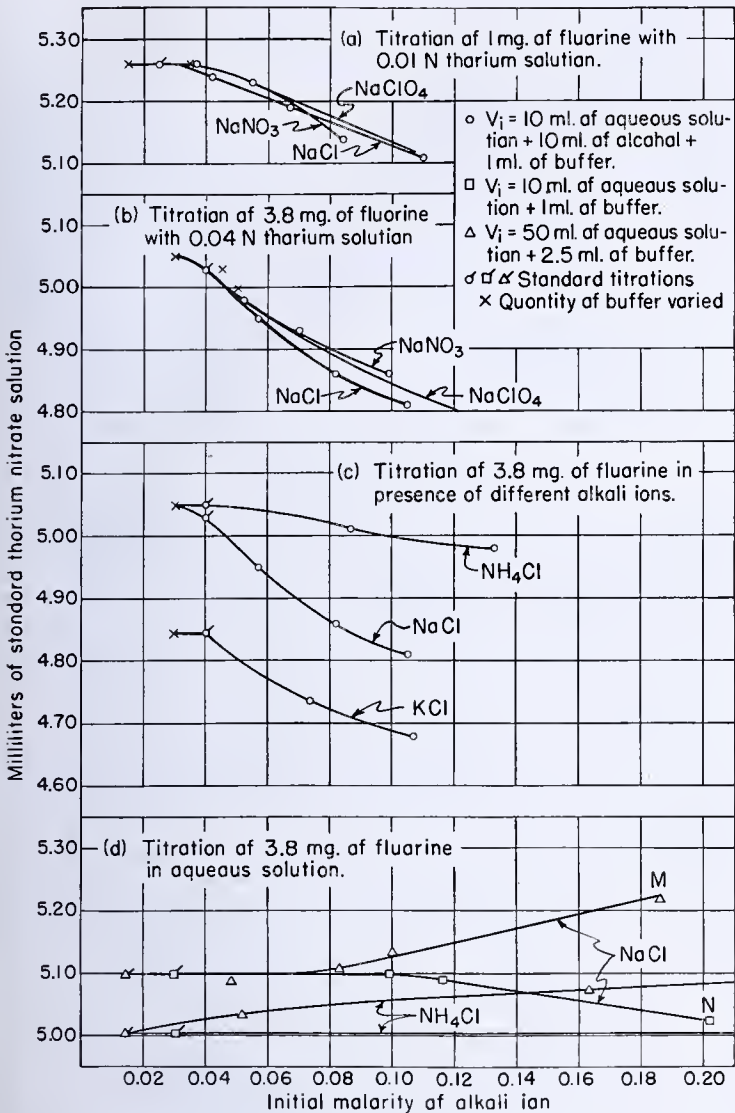


FIGURE 2. EFFECT OF ALKALI CHLORIDES, NITRATE, AND PERCHLORATE ON THE TITRATION OF ALKALI FLUORIDE WITH THORIUM NITRATE

Certain ions, such as chloride, nitrate, and perchlorate, cause low results in alcoholic solution, whereas others, such as sulfate and orthophosphate, give rise to high results. Furthermore, the effects of chloride, nitrate, and perchlorate are quantitatively very much the same, which suggests the possibility of the accompanying alkali ion being the principal source of the interference. If this be true, account must be taken of the alkali ion introduced in the fluorine salt and in the buffer. Accordingly, the effects of the ions are shown graphically (Figure 2) by plotting the titers against the molarity of the alkali ion at the beginning of the titration. For titrations in alcoholic solution the concentration is reckoned on the basis of the aqueous solution before the addition of alcohol.

With 1 mg. of fluorine in alcoholic solution (Figure 2, a) the salt effect becomes noticeable at about 0.03 M, or less than one-third of the concentration reported (16) to be permissible in the titration of approximately 0.05 mg. of fluorine in 50 ml. of alcoholic solution, and with 3.8 mg. of fluorine about the same threshold concentration is indicated (Figure 2, b). Accordingly, the concentrations of sodium ion in which sodium fluoride is usually titrated (standard titrations, Figure 2) are below (Figure 2, a) or above (Figure 2, b) the threshold of interference in alcoholic solution, depending upon the quantity of fluorine that is involved. Moreover, alteration of the sodium concentration by varying the volume of buffer also gave results (Figure 2, b) that follow the course of the curves for the other salts. These variations in

the amount of buffer had only a slight effect on the pH of the titrated solution (Table I). The observation that the addition of these salts to the solution towards the end of the titration produces little or no effect on the titer indicates that the interference arises from reactions that occur during the initial stages of the titration when the fluoride concentration is greatest.

As a probable explanation of the effect of sodium ion the formation of insoluble compounds, such as Na<sub>2</sub>ThF<sub>6</sub> (13, p. 606), suggests itself; thus the possibility of potassium or ammonium salts causing less interference than sodium salts becomes apparent. To investigate this point a dilute solution of hydrofluoric acid was prepared and adjusted to a suitable concentration by titration with thorium solution in the customary manner, and standard solutions of potassium fluoride and ammonium fluoride were prepared by neutralizing aliquots of this solution. Aliquots (3.8 mg. of fluorine) of these standard fluoride solutions, with and without the addition of alkali chloride, were titrated with thorium nitrate, using a buffer prepared from the respective alkali hydroxide. The results are plotted in Figure 2, c, and for comparison the sodium chloride curve (Figure 2, b) is reproduced. The ammonium ion interferes to a much less extent than the sodium ion. In the potassium system the standard titration is considerably lower than the corresponding titer in the sodium system; furthermore, the effect of added alkali chloride is also somewhat less.

TABLE I. EFFECT OF BUFFER CONCENTRATION, ALKALI-ION CONCENTRATION AND NATURE OF ALKALI ION ON pH OF TITRATED SOLUTION

Fluorine Present Mg.	Alkali System <sup>a</sup>	Alkali Chloride Added Mg.	Volume of Buffer Solution Ml.	Titer in Terms of 0.04 N Thorium Solution Ml.	pH of Titrated Solution <sup>b</sup>
Titration in Alcoholic Solution <sup>c</sup>					
3.8	Sodium	None	0.5	5.05	3.29
3.8	Sodium	None	1.0	5.03	3.30
3.8	Sodium	None	2.0	5.02	3.24
3.8	Sodium	50	1.0	4.81	3.28
3.8	Potassium	None	1.0	4.85	3.40
3.8	Ammonium	None	1.0	5.05	3.50
3.8	Ammonium	50	1.0	4.98	3.40
Titration in Aqueous Solution <sup>d</sup>					
1.0	Sodium	None	2.5	1.40	2.86
3.8	Sodium	None	1.25	5.02	2.92
3.8	Sodium	None	2.5	5.09	2.82
3.8	Sodium	None	5.0	5.10	2.78
10.0	Sodium	None	2.5	13.35	2.87
3.8	Sodium	1,000	2.5	5.21	2.80
3.8	Potassium	None	2.5	4.97	2.90
3.8	Ammonium	None	2.5	5.00	3.00
3.8	Ammonium	1,000	2.5	5.14	2.90

<sup>a</sup> Sodium (or potassium or ammonium) ion was the only alkali ion present in the solution.  
<sup>b</sup> Determined with the glass electrode by L. M. White of this bureau.  
<sup>c</sup> Initial volume was 10 ml. of aqueous solution, 10 ml. of alcohol, and the indicated volume of buffer.  
<sup>d</sup> Initial volume was 50 ml. of aqueous solution and the indicated volume of buffer.

In aqueous solution the interference effects of alkali chlorides, nitrates, and perchlorates become noticeable (Figure 2, d) when the total initial sodium concentration is 0.08 to 0.1 M, depending upon the initial volume of the titrated solution, or about three times the threshold concentration in alcoholic solution. In the larger volume the titer in both the sodium and the ammonium systems was increased by relatively large quantities of alkali chloride (Figure 2, d), whereas low titers were observed in the other cases (Figure 2). In contrast to the type of salt interference that gives rise to low results, this effect, observed to be more general in the system of ammonium salts, is not lessened when the addition of alkali chloride is withheld until the titration is nearly completed. Moreover, it does not appear to be attributable to pH effects—for example, after titration



both solutions M and N (Figure 2, *d*) had a pH value of 2.90 (glass electrode).

Of the negative ions that cause high results the orthophosphate and sulfate ions were investigated (Figure 3). Orthophosphate ion apparently titrates quantitatively, an observation also noted by Hoskins and Ferris (16), and must be excluded when titrating in alcoholic solution (Figure 3, *a*). With aqueous solutions the situation is improved a little, in which case the presence of the equivalent of 0.1 mg. of  $\text{PO}_4^{---}$  would be expected to cause less than 1 per cent error for amounts of fluorine in excess of 1 mg. when the initial volume is 50 ml.

The interference of sulfate in alcoholic solution depends upon the amount of fluorine present (Figure 3, *b*), as is also indicated by recent data of others (10). Sulfate interference has been attributed (16) on the basis of conductivity data to the slight dissociation of thorium sulfate even in very dilute solution. The fact that sulfate also causes high results in the gravimetric determination of fluorine as thorium fluoride (11) suggests the formation of an insoluble compound of the type  $\text{ThF}_2\text{SO}_4$ . On the other hand, in titrations made in aqueous solution sulfate interference disappears almost entirely (Figure 3, *b*), and the small disturbing action that remains (error of 0.015 mg. of fluorine for 2 mg. of  $\text{SO}_4^{--}$ ) appears to be independent of the volume.

The effects of a few other substances on the titration were studied briefly. In alcoholic solution (3.8 mg. of fluorine) the presence of 1 mg. of boron trioxide caused no trouble, and 5 mg.

produced only a small increase in the titer, whereas 20 mg. were without effect in aqueous solution. With 1 mg. of fluorine in alcoholic solution 1.3 mg. of  $\text{S}^{--}$  had no effect, though 6.6 mg. lowered the titer about 0.1 ml. The titration of 3.8 mg. of fluorine in alcoholic solution was not affected by the presence of 10 mg. of  $\text{AsO}_3^{---}$ . The addition of 15 mg. of silicon dioxide, the largest amount tried, in the form of a solution of sodium silicate had no effect on the titration of 3.8 mg. of fluorine in 50 ml. of aqueous solution. Under the same conditions of titration 40 mg. of  $\text{ClO}_3^-$  added as the sodium salt were without effect. On the other hand, 2.5 mg. of  $\text{ClO}^-$  caused the indicator to fade rapidly. This fading of the indicator was not observed with solutions containing added hypochlorite that had been evaporated to 5 ml. and diluted to 50 ml. before titration. The interference of free chlorine has been noted by Lockwood (18).

### Separation of Fluorine from Interfering Substances

Distillation with a nonvolatile acid is the most satisfactory method for isolating fluorine from natural phosphates. Phosphoric, sulfuric, and perchloric acids are available for this purpose. The effectiveness of these acids in the isolation of fluorine from various types of materials has been studied by Reynolds (21), Dahle and Wichman (6, 7, 8), and Churchill *et al.* (3).

**CHOICE OF ACID FOR DISTILLATION.** The use of phosphoric acid for the distillation of fluorine from phosphate materials has been frowned upon, because the distillates always contain phosphoric acid, in amount often sufficient to interfere in the subsequent titration (21). Phosphoric acid

is useful, however, with materials that contain notable amounts of easily oxidizable organic matter, with which the use of perchloric acid would be unsafe. The phosphoric acid distillate may, where experience shows this course to be worth while, be redistilled with perchloric acid for complete separation of the phosphorus.

According to the experience of this laboratory, the use of sulfuric acid as a distilling agent for phosphate rock results in poor recovery of fluorine when the distillation temperature is maintained below  $150^\circ\text{C}$ . At a higher temperature complete expulsion of the fluorine from fused sodium carbonate samples is attainable (15) at the expense of contamination of the distillate with sulfuric acid.

On account of high solubility of its salts perchloric acid is the most satisfactory distilling acid, though considerable care should be exercised in its use directly on samples that contain notable amounts of organic matter. A hazard not always recognized resides in the use of rubber stoppers in the distilling flask. Phosphoric acid has not been found in the perchloric acid distillates of 0.1-gram samples of phosphate rock (21). With large samples of phosphate-rich material in the distilling flask the distillate does carry more or less orthophosphate (3, 21). Furthermore, according to recent observations in this laboratory, perchloric acid distillates obtained with the aid of stills in which phosphoric acid had been used as a distilling agent also contain appreciable quantities of phosphate. Thus, it appears desirable to provide separate equipment for the use of phosphoric acid.

After distillation with perchloric acid the fluorine is accompanied by a small amount of the distilling acid, as well as a small amount of phosphoric acid under certain conditions, by practically all of the hydrochloric and nitric acids in the sample, and by sulfur compounds in the case of pyritiferous samples. Boron also distills in part, and arsenic may be expected under certain conditions. The distillate

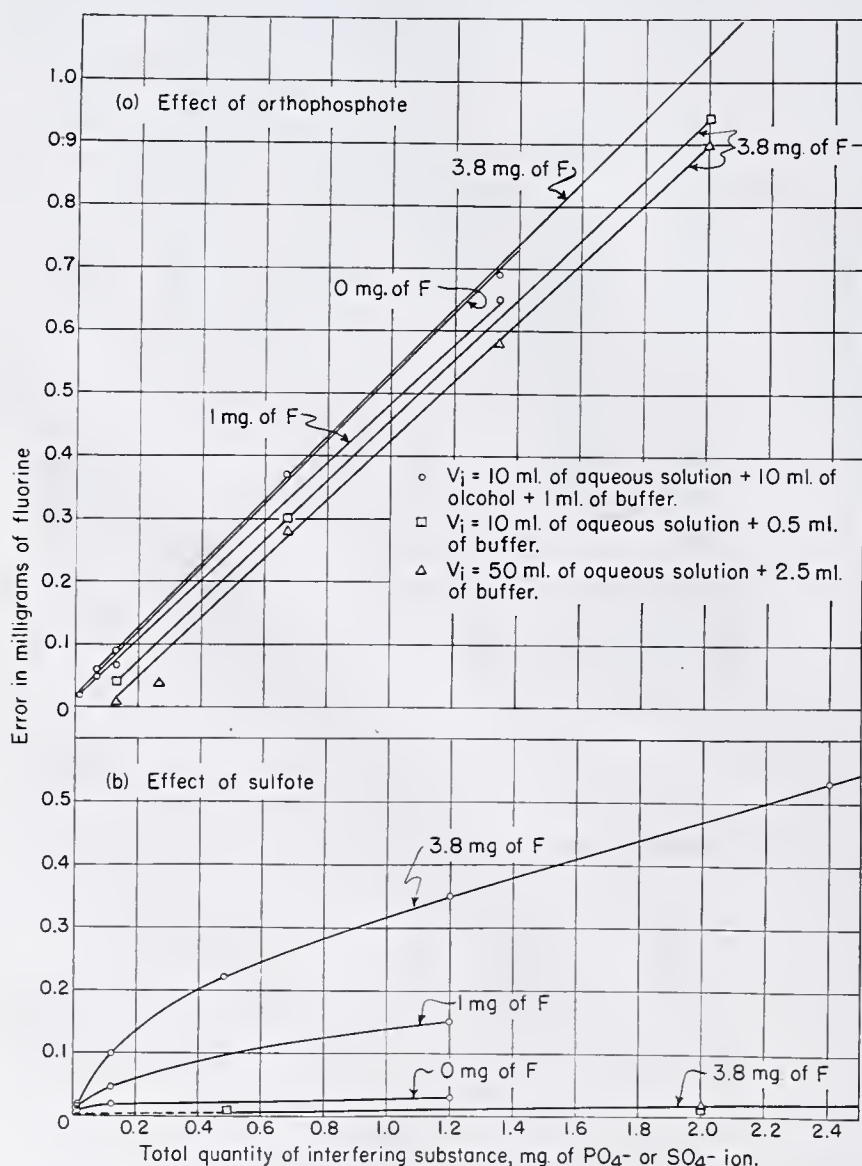


FIGURE 3. EFFECT OF ORTHOPHOSPHATE AND SULFATE IONS ON TITRATION OF SODIUM FLUORIDE WITH THORIUM NITRATE



(150 ml.) from 0.1 gram of phosphate rock and 0.05 gram of borax contained 5 mg. of boron trioxide. Although all these elements may be encountered in phosphatic materials, pyritic sulfur alone assumes importance in phosphate rock analysis, as the quantities of the other elements present in the sample are below the limits of interference shown above for titration in aqueous systems.

SUBSTANCES THAT RETARD THE DISTILLATION OF FLUORINE. Gelatinous silica (28) and large quantities of soluble aluminum salts (7) retard the rate of distillation of fluorine, but the quantities of these substances usually encountered in commercial phosphate rock are insufficient to interfere seriously. Silicates that are decomposed by acid also cause difficulty by forming on the interior of the flask a coating of precipitated silica, which is capable of retaining fluorine during the distillation of fluorine-rich samples only to give it up, at least in part, during subsequent distillations of samples less rich in fluorine, thereby vitiating the results in both instances (21). This coating of precipitated silica, which would ordinarily be mistaken for etching, is readily removed by treatment with hot concentrated alkali solution.

TABLE II. EFFECT OF EVAPORATION OF SODIUM FLUORIDE SOLUTION ON TITER WITH THORIUM NITRATE

(Solution was evaporated to 40 to 45 ml.  $V_1 = 50$  ml. of aqueous soln.)

Series Added No. Fluorine <sup>a</sup> Mg.	Procedure	Approximate Volume of Solution at Beginning of Evaporation ML.	Duplicate Experiments in Terms of 0.04 N Thorium Solution ML.
1	1.0	Direct titration	Not evaporated 1.39, 1.41
		Plus water 150	1.40, . .
		Plus water + 0.05 mg. of SiO <sub>2</sub> <sup>b</sup> 150	1.40, 1.40
		Distilled with HClO <sub>4</sub> to volume of 150 ml. 150	1.41, 1.42
2	3.8	Direct titration	Not evaporated 5.08, 5.10
		Plus water 300	5.08, 5.10
		Plus water + 1.9 mg. of SiO <sub>2</sub> <sup>c</sup> 150	5.02, 5.03
		Plus water + 3.8 mg. of SiO <sub>2</sub> 150	5.01, 5.03
		Plus water + 7.6 mg. of SiO <sub>2</sub> 150	4.98, 4.96 <sup>d</sup>
3	3.8	Distilled with HClO <sub>4</sub> to volume of 150 ml. 150	4.98, 5.00
		Plus 150 ml. of HClO <sub>4</sub> distillate (blank) + 1.9 mg. of SiO <sub>2</sub> <sup>c</sup> 150	5.00, 5.00
4	10.0	Distilled with HClO <sub>4</sub> to volume of 150 ml., made up to 250 ml., and titrated 50-ml. aliquots (2 mg. of F) 150	2.63, 2.72 2.58, 2.68
5	20.0	Same as series 4. Aliquots = 4 mg. of F 150	5.25, 5.30 5.25, 5.23

<sup>a</sup> Aliquots of standard sodium fluoride solutions were used.

<sup>b</sup> Silica was added in the form of a clear solution of Na<sub>2</sub>SiO<sub>3</sub>.

<sup>c</sup> Approximately the SiO<sub>2</sub> equivalent of the fluorine as H<sub>2</sub>SiF<sub>6</sub>.

<sup>d</sup> Indistinct end point.

EVAPORATION OF FLUORINE-CONTAINING SOLUTIONS. In the analytical determination of fluorine it is frequently convenient, if not absolutely necessary, to reduce the relatively large volume of neutralized distillate by evaporation. In view of the limited size of sample (0.1 gram) heretofore considered practical in phosphate rock analysis concentration seemed desirable, in order to have as much as 3 to 4 mg. of fluorine for titration with thorium nitrate solution. Moreover, concentration seemed permissible on the basis of comparative results obtained on phosphate rock. More recently, as the result of efforts to locate the cause of low recovery of fluorine in the distillates of sodium fluoride, it has been found that under certain conditions, illustrated by typical data in Table II, evaporation of alkaline (phenolphthalein) fluorine-containing solutions leads to low titers with thorium nitrate solution.

When the involved quantity of fluorine was 1 mg., evaporation had no observable effect on the result (Table II, series 1). The lowered titers of larger quantities of fluorine seem to be traceable to the influence of soluble silica (series 2), although

the presence of moderate amounts of soluble silica in un-evaporated solutions does not affect the titer, and the effect of evaporation on the titer of aliquots of distillates (series 4 and 5) is attributable, at least in part, to the effect of the silica from the distilled fluosilicic acid. The reactions responsible for the lowered titer have not been determined. However, the addition of evaporated blank distillates from perchloric acid, which presumably carry only traces of soluble silica, also lowered the titer of standard sodium fluoride. The latter effect is briefly discussed in the following section.

TABLE III. EFFECT OF EVAPORATION OF DISTILLATES FROM PHOSPHATE ROCK ON TITER WITH THORIUM NITRATE

Sample No.	Type or Source of Phosphate	Titer of Solutions from 0.1 Gram of Sample <sup>a</sup>		
		A ML.	B ML.	C ML.
120 <sup>b</sup>	Florida land pebble	4.94 4.97	4.90 4.93	4.94 4.97
56a <sup>b</sup>	Tennessee brown rock	4.74 4.76	4.69 4.71	4.74 4.71
930	Tennessee blue rock	4.61 <sup>c</sup> 4.63	4.60 <sup>c</sup> 4.57	4.58 <sup>c</sup> 4.58
948	Wyoming	4.63 <sup>c</sup> 4.62	4.60 <sup>c</sup> 4.60	4.63 <sup>c</sup> 4.65
1253	Idaho	4.31 4.30	4.27 4.27	4.34 4.31

<sup>a</sup> In procedure A the 150-ml. perchloric acid distillate of a 1-gram sample was made up to 250 ml., from which a 25-ml. aliquot was taken, diluted to 50 ml., and titrated in aqueous solution. Procedure B is the same as A, except that the aliquot was diluted to 150 ml. and then evaporated to 45 to 50 ml., whereas in C the 150-ml. distillate of 0.1 gram of the rock was evaporated to 45 to 50 ml.

<sup>b</sup> National Bureau of Standards standard sample.

<sup>c</sup> Distilled in the presence of KMnO<sub>4</sub>.

The titers (corresponding to 0.1-gram samples) of phosphate rock distillates show an observable lowering as a result of evaporation (Table III). The small differences (0.03 to 0.04 ml. of 0.04 N thorium solution), however, amount to only 0.02 to 0.03 per cent of the sample.

TABLE IV. THORIUM NITRATE CONSUMED BY BLANK DISTILLATES FROM PERCHLORIC ACID<sup>a</sup>

Series No.	Procedure <sup>b</sup>	Total Titers of Duplicate Experiments in Terms of 0.01 N Thorium Solution ML.
1	Titration blank 150 ml. of distillate from water alone 150 ml. of distillate from HClO <sub>4</sub> No. 1 150 ml. of distillate from HClO <sub>4</sub> No. 2	0.11, 0.10 0.10, 0.14 0.35, 0.33 <sup>c</sup> 0.22, 0.20, 0.22 <sup>c,d</sup>
2	150 ml. of a 300-ml. HClO <sub>4</sub> (No. 1) distillate 150 ml. of same distillate after evaporation and redistillation (150 ml.)	0.35, 0.35 0.68, 0.67

<sup>a</sup> 10 ml. of 60 per cent perchloric acid and 5 ml. of water were added to distilling flask.

<sup>b</sup> All titrations were made in a volume of 10 ml. of aqueous solution. Neutralized distillates were evaporated to 5 to 10 ml.

<sup>c</sup> Results are for consecutive 150-ml. portions.

<sup>d</sup> When titration medium was 50 per cent ethanol (20 ml.) corresponding results were 0.13, 0.14, and 0.12 ml.

BLANK ON PERCHLORIC ACID. The distillate obtained from perchloric acid without added fluorine consumes more thorium nitrate than is required by the titration blank, and the amount varies with different lots of acid and with the volume of the distillate (Table IV). Eberz *et al.* (10) made similar observations and recommended that the acid be purified by continued distillation until the blank became zero. Noteworthy in this connection is the near constancy of the titers of three successive 150-ml. distillates from one lot of acid (series 1). Furthermore, the blank appears to accumulate in double distillation (series 2). On the other hand, by far the larger part of this blank is evidently due to something other than fluorine, because the addition of the evaporated blank distillate to a known amount of sodium fluoride solution, oddly enough, gives rise to a slightly lowered titer. This tendency towards a negative effect on the titration may also be noted by comparing the results in Table II (series 2 and 3).



RECOVERY OF FLUORINE BY DISTILLATION WITH PERCHLORIC ACID. The recovery of fluorine from solutions of sodium fluoride by distillation with perchloric acid and titration of unevaporated distillates was 100 per cent with amounts of fluorine ranging from 1 to about 15 mg. The apparent recovery shown by the titers of evaporated distillates was nearly constant (99 per cent) over the range 3 to about 15 mg. Below about 3 mg. of fluorine the effect of evaporation decreases (Figure 4, *a*) and becomes negligible at 1 mg., as is indicated in Table II. Above 15 mg. of fluorine the recovery was variable. In view of the fact that this behavior was not observed in the results for phosphate rock, the variable recovery of the larger quantities of fluorine from sodium fluoride was not investigated further.

TABLE V. FLUORINE IN PERCHLORIC ACID DISTILLATES OF TYPICAL PHOSPHATE ROCKS BY DIFFERENT METHODS OF ANALYSIS

(Weight of sample, 1 gram. Volume of distillate, 150 ml.)

Sample No.	Type or Source of Phosphate	Fluorine Found	
		Thorium nitrate titration <sup>a</sup>	Lead chlorofluoride method (15)
		%	%
120 <sup>b</sup>	Florida land pebble	3.70	3.74
		3.71	3.72
56a <sup>c</sup>	Tennessee brown rock	3.54	3.47
		3.55	3.55
930	Tennessee blue rock	3.44 <sup>d</sup>	3.53
		3.46	3.58
1253	Idaho rock	3.21	3.26
		3.20	3.29

<sup>a</sup> Aliquot of distillate was titrated directly in an initial volume of 50 ml. of aqueous solution.

<sup>b</sup> National Bureau of Standards standard sample No. 120. Certificate value for fluorine 3.76%.

<sup>c</sup> National Bureau of Standards standard sample No. 56a. Certificate value for fluorine 3.56%.

<sup>d</sup> Results obtained by distillation in presence of potassium permanganate.

That the recovery of fluorine from phosphate rocks is independent of the quantity of fluorine in the investigated range, 3 to about 40 mg., is shown by the linear relationship between the thorium nitrate titers of evaporated distillates (not aliquoted) and the weight of sample distilled (Figure 4, *b*). The results (Table V) obtained on perchloric acid distillates of typical phosphate rocks by titration with thorium nitrate and by the lead chlorofluoride method (14) agree very closely. That substantially complete recovery was realized is indicated by the fact that the results thus obtained on 1-gram samples of the National Bureau of Standards standard samples are only slightly different from the certified values for these samples. Perchloric acid distillation gave low results (0.2 to 0.3 per cent) on phosphate rock samples that had been fused with sodium carbonate. On the other hand, Hoffman and Lundell (15) found that a preliminary fusion with sodium carbonate improved the recovery when sulfuric acid was the distilling acid.

The entire distillate may also be titrated without resorting to evaporation. The blank correction to the titer, however, appears to vary with the type of phosphate. This condition is indicated by the intercepts of the curves with the zero ordinate in Figure 4, *c*, where only a part of the investigated range is shown.

ELIMINATION OF THE EFFECT OF PYRITIC SULFUR. As already indicated, perchloric acid distillates of pyritiferous phosphates, such as Tennessee blue rock, carry sulfur in some form. In the case of samples containing 3 to 5 per cent (as sulfur trioxide) of pyritic sulfur the determined quantity of total sulfur in 150 ml. of distillate from 0.1 gram of sample ranged from 1 to 3 mg. of sulfur trioxide. Approximately half of that distilled was in the sulfate condition after the distillate had been neutralized and evaporated to a volume of 10 ml. The milkiness of the distillates, which disappears upon neutralization and evaporation, is probably due to free

sulfur. Only a trace of hydrogen sulfide could be detected at the condenser exit during distillation.

The quantities of sulfate sulfur found in the evaporated distillates of pyritiferous samples are sufficient to produce serious error in the results obtained by titration in an alcoholic solution (Figure 3, *b*), and the error, though greatly reduced, is not entirely eliminated by titration in an aqueous system. Separation of the sulfur from fluorine can be made much more complete in one distillation by adding permanganate to the distilling flask before starting the distillation, and its use in the absence of more than traces of chloride seems to be entirely unobjectionable. An excess of permanganate should be used. Although the amount needed will depend upon the quantity of oxidizable substance in the sample, the authors have found 5 ml. of a saturated solution of potassium permanganate to provide a sufficient excess for 1-gram samples of phosphate rock. Accordingly, the sample after transfer to the distilling flask is moistened with the permanganate solution, perchloric acid is then added, and the distillation is conducted in the usual manner. When an excess of permanganate is used, the residue from the distillation is black.

Results for fluorine in a number of pyritiferous and pyrite-free phosphates by distillation with and without permanganate and titration in alcoholic and aqueous solutions are

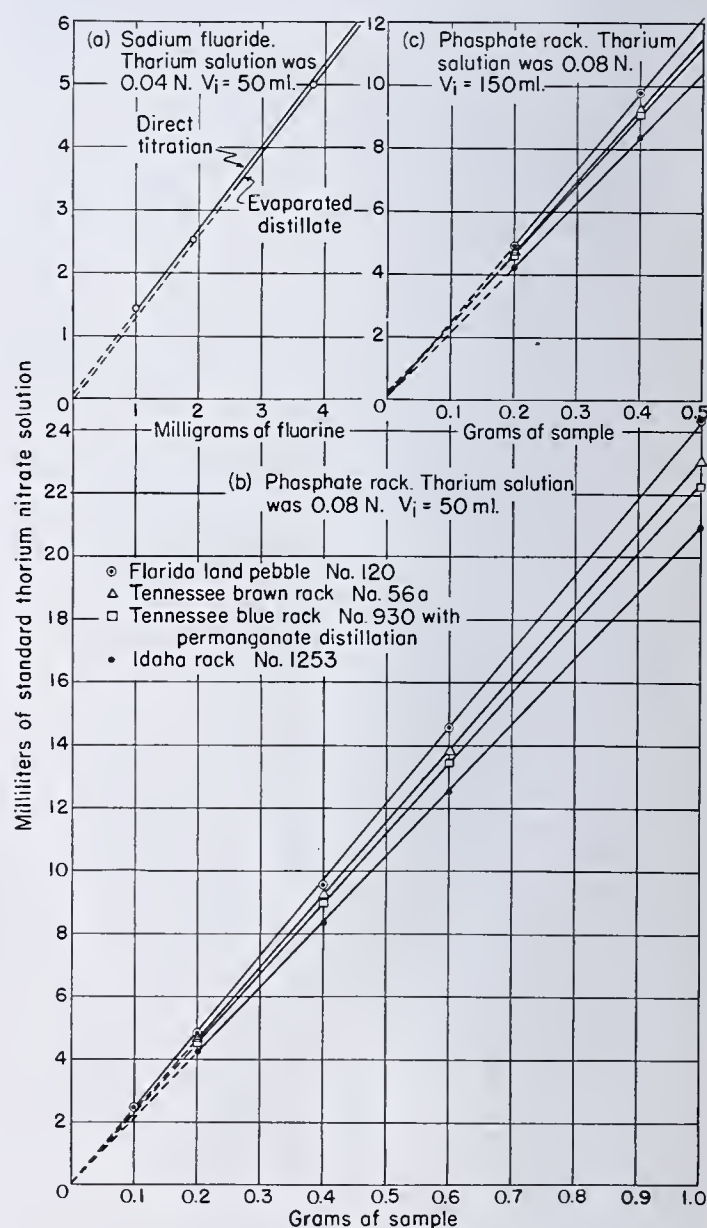


FIGURE 4. RECOVERY OF FLUORINE FROM SODIUM FLUORIDE AND PHOSPHATE ROCK

By distillation with perchloric acid and titration in aqueous solution with thorium nitrate. Volume of distillate, 150 ml.



TABLE VI. FLUORINE IN PYRITIFEROUS AND PYRITE-FREE PHOSPHATES

Sample No.	Type or Source of Phosphate	P <sub>2</sub> O <sub>5</sub>	Organic C <sup>a</sup>	Pyritic Sulfur as SO <sub>3</sub> <sup>a</sup>	Fluorine Determined <sup>b</sup>			
		%	%	%	D	E	F	G
120 <sup>c</sup>	Florida land pebble	35.25	0.32 <sup>d</sup>	<0.02	3.71	3.70	3.71	3.69
912	Sample 120 + FeS <sub>2</sub>	...	...	5.34	4.27	3.87	3.72	3.70
56a <sup>c</sup>	Florida land pebble	35.37	0.38	<0.02	3.71	3.68	3.69	3.69
56 <sup>c</sup>	Tennessee brown rock	32.82	0.26 <sup>d</sup>	<0.02	3.53	3.53	3.56	3.54
448	Tennessee brown rock	31.28	0.25	1.19	3.58	3.43	3.44	3.45
1049	Tennessee blue rock	32.03	...	1.37	3.72	3.49	3.50	3.58
772	Tennessee blue rock	31.22	1.46	2.02	3.23	3.12	3.03	3.06
449	Tennessee blue rock	30.45	0.36	2.71	3.51	3.27	3.25	3.22
930	Tennessee blue rock	33.65	...	3.19	4.17	3.82	3.76	3.75
1138	South Carolina land rock	30.97	0.20	5.21	3.98	3.51	3.42	3.49
948	Wyoming, Cokeville	27.85	0.51	0.46	3.63	3.55	3.53	3.49
1253	Idaho, Conda	30.19	2.69	1.30	3.60	3.45	3.46	3.47
1012	Montana, Garrison	32.13	>2	<0.02	3.30	3.23	3.22	3.23
1011	Montana, Garrison	36.07	<0.2	<0.02	4.54	4.42	4.42	4.42
		27.63	>0.2	<0.02	6.93	6.79	6.83	6.84

<sup>a</sup> Unless indicated otherwise, results unaccompanied by inequality sign are those given by Jacob *et al.* (17).

<sup>b</sup> In procedure D a 150-ml. distillate of 0.1 gram of rock was evaporated to 10 ml. and titrated in 20 ml. of 50 per cent ethanol; in E a 150-ml. distillate of 0.1 gram of rock was evaporated to 45 to 50 ml. and titrated in this volume of aqueous solution; F is same as E with permanganate distillation; in G 0.5 gram of rock was distilled with permanganate, the 150-ml. distillate was made up to 250 ml., and fluorine was titrated in an unevaporated 50-ml. aliquot.

<sup>c</sup> Bureau of Standards standard sample of phosphate rock.

<sup>d</sup> Reported as organic matter by Hoffman and Lundell (15).

TABLE VII. FLUORINE IN IGNITED PHOSPHATE ROCKS

Sample No.	Type or Source of Phosphate	Organic C <sup>a</sup>	Pyritic Sulfur as SO <sub>3</sub> <sup>a</sup>	Fluorine		Difference %
		%	%	Ignited sample <sup>b</sup>	Unignited sample <sup>c</sup>	
120 <sup>d</sup>	Florida land pebble	0.32 <sup>e</sup>	<0.02	3.71	3.71	±0.00
...	Sample 120 + FeS <sub>2</sub>	...	5.34	3.31	3.72	-0.41
56a <sup>d</sup>	Tennessee brown rock	0.26 <sup>e</sup>	<0.02	3.49	3.56	-0.07
56 <sup>d</sup>	Tennessee brown rock	0.25	1.19	3.35	3.44	-0.09
449	Tennessee blue rock	...	3.19	3.55	3.76	-0.21
930	Tennessee blue rock	0.20	5.21	3.24	3.42	-0.18
948	Wyoming, Cokeville	2.69	1.30	3.40	3.46	-0.06
1253	Idaho, Conda	>2	<0.02	3.16	3.22	-0.06

<sup>a</sup> See footnote <sup>a</sup>, Table VI.

<sup>b</sup> Sample was heated in a muffle furnace at 500° C. for 0.5 hour; its fluorine content was then determined by procedure E (Table VI).

<sup>c</sup> Fluorine was determined by procedure F (Table VI).

<sup>d</sup> Bureau of Standards standard sample of phosphate rock.

<sup>e</sup> Reported as organic matter by Hoffman and Lundell (15).

given in Table VI. At the time these analyses were made samples larger than 0.1 to 0.2 gram had not been shown to be permissible, which accounts for the small samples used. The effect of pyrite on the result for fluorine, as well as the usefulness of permanganate in its presence, can be most readily observed by comparing the results for Florida land pebble 120 with and without added pyrite.

Hoffman and Lundell (15) mention a collaborator's suggestion that the effect of pyrite can be eliminated by igniting the sample prior to distillation. Data obtained in this laboratory (Table VII) show that this treatment causes low results when the sample contains pyrite.

Other uses for permanganate distillation are worthy of mention in this connection. Organic substances have been observed in the distillate of certain research samples that contained cottonseed meal, in which cases the results for fluorine were low. With the use of permanganate, however, satisfactory results were obtained on these materials. Dahle (4) separated fluorine from large amounts of chloride by refluxing with sulfuric acid and permanganate prior to the distillation of the fluorine. The authors have used double distillation with perchloric acid and permanganate to separate fluorine from moderately large amounts of chloride.

### Procedure for Determining Fluorine in Phosphate Rock

For accurate and consistent results the authors suggest the following procedure:

Distill 0.5 gram of the sample and 15 ml. of perchloric acid (2 + 1) at 125° to 150° C., preferably in a steam-distillation

unit (24), until the volume of the distillate is 150 ml. If the material is pyritiferous, moisten the sample in the distilling flask with 2 to 3 ml. of a saturated solution of potassium permanganate and increase the concentration of the added perchloric acid accordingly. Neutralize (phenolphthalein) the distillate with 1 M sodium hydroxide and make it up to a volume of 250 ml. To a 50-ml. aliquot of this solution add 5 drops of alizarin indicator (0.1 per cent aqueous solution of sodium alizarin sulfonate) and 0.1 M hydrochloric acid until the pink of the alizarin is discharged. Now add 2.5 ml. of monochloroacetic acid (0.4 M)-sodium hydroxide (0.2 M) buffer solution and titrate with 0.04 N thorium nitrate solution. The end point is very sharp. About 1 hour is required for a determination.

Correct the titer by deducting the titration blank found by titrating a series of sodium fluoride solutions covering the range of the amounts of fluorine involved in the analysis. On account of the lowering effect of added blank perchloric acid distillates on the titer of sodium fluoride, this blank correction is slightly greater than the true blank.

For control work in which the highest attainable accuracy is not necessary the procedure can be shortened by distilling 1 gram of rock to a volume of 150 ml. and titrating the distilled fluorine directly in this volume with 0.08 N thorium solution, using 15 drops of indicator solution and 7.5 ml. of buffer solution. Since the end point is not sharp, a standard for comparison is desirable.

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# Improvement of Vacuum Distillation

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OBTAINING substances of perfect purity is of the greatest importance in both chemical and physical investigations. When fractionating devices based on the Anschütz-Thiele apparatus are used for vacuum distillation, the purity of the fractions received is doubtful, because of the necessity of greasing the stopcock through which the distillate passes. Using other devices without this fault, distillation cannot be controlled without interrupting the process, which is inconvenient. This difficulty may be easily avoided by using the fractionating contrivance shown in Figure 1.

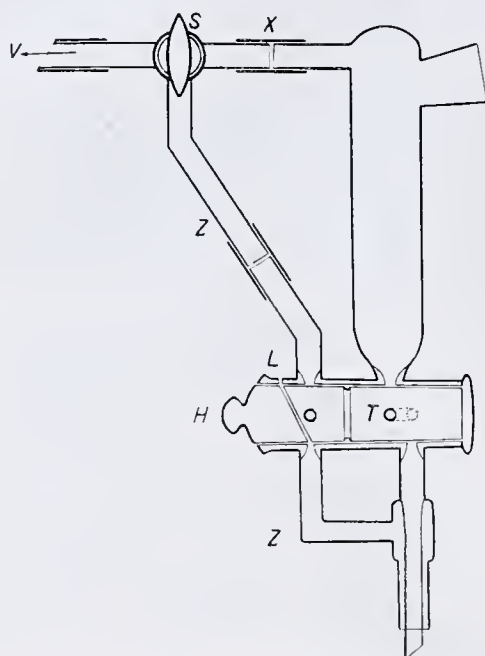


FIGURE 1. FRACTIONATING DEVICE

L. Hole to let in air  
V. To vacuum pump

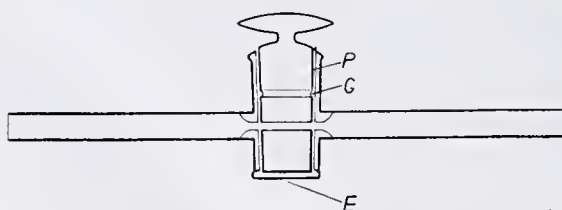


FIGURE 2. STOPCOCK

G. Groove  
P. Greased part of stopcock  
E. Sealed side of shell

A stopcock is fitted to this contrivance, the simplest form of which is shown in Figure 2. The plug of the stopcock has a groove, and its exterior is sealed at one side. The plug is greased only in the upper (broader) part of the groove, and the groove prevents dispersion of grease to its narrower part, which in the device described is greased by the distillate.

The manipulation of this device (Figure 1) is simple: The three-way stopcock, *S*, is so arranged that while the distillate is being collected it is evacuated with pump only through tubes *ZZ*, but during exchange of the receiving flask it is evacuated through connections *X*. The hole, *T*, of stopcock *H* is diagonal, for after exchange of the receiving flask it is possible, by suitably adjusting this stopcock and stopcock *S*, to remove air from the new receiver without disturbing the distillation.

The stopcock may also be applied to other apparatus, to avoid contamination usually caused by greasing whole plugs—in stopcocks which join tubes filled with mercury, etc. The

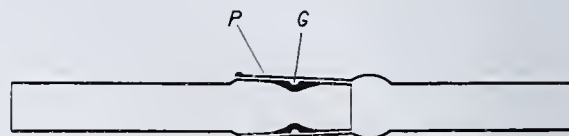


FIGURE 3. CONNECTION TUBES WITH GROUND JOINT

G. Groove  
P. Greased part of joint

inner parts of connection tubes with ground joints should also be provided with grooves (Figure 3), as leaking of grease out of the joint is always undesirable.

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## Direct Titration of Sulfate

### Erythrosin as Internal Indicator

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DURING recent years several suggestions concerning the use of adsorption indicators for the volumetric determination of sulfate have been advanced.

Wellings (6) reported that, in the presence of magnesium or manganous ions, fluorescein can be used as an internal indicator for the direct titration of sulfate with barium hydroxide. His results indicate an average relative error of somewhat less than 0.5 per cent. However, according to Iyer (2), the end point of this titration is not very sharp. Moreover, nitrate ions were found to interfere with the operation of the indicator, a fact that is the more serious since a removal of these ions would render the determination very complicated. Essentially different from Wellings' method is the one suggested by Roy (5), who mentioned the possibility of using fluorescein as an external indicator for the indirect titration of sulfate with lead nitrate and potassium sulfate. Though, to the author's knowledge, no data concerning a practical application of this method have been presented, it appears certain that such a determination would be rather time-consuming. In 1936 Ricci (4) published a study of the direct titration of sulfate with lead nitrate in the presence of eosin as internal indicator, reporting an average relative error of 0.33 per cent in 65 analyses of sodium sulfate solutions. In a discussion of the effect of variations he stated that if the final volume of solution is much above 30 ml. it is difficult to detect the end-point change, and pointed out that efforts to sharpen the end point by the addition of alcohol did not meet with success. According to Ricci only small percentages of this diluent can be tolerated, while the presence of more alcohol delays the end point so much that the titration becomes impossible.

### Erythrosin as Indicator

It was during a study of the properties of erythrosin (tetraiodofluorescein) that the very low solubility and characteristic violet-red color of its lead salt suggested to the author the possibility of using it as an internal indicator for the direct titration of sulfate with lead nitrate. However, the conditions under which this indicator works best are very different from those recommended for the eosin method. Preliminary experiments revealed that in the titration of sulfate with lead nitrate the replacement of eosin by erythrosin



causes the color change to start long before the equivalence point is reached. In order to render erythrosin useful as an indicator for this titration, it proved necessary to modify the relationship between the solubilities of lead sulfate and lead erythrosinate to a considerable extent. The influence of ethyl alcohol on the solubilities of these two compounds suggested that this diluent might be added to the solution to be titrated, to bring about a correct end point.

TABLE I. TITRATION OF SULFATE

No.	SO <sub>4</sub> Present Gram	SO <sub>4</sub> Found Gram	Error %
1	0.0482	0.0483	+0.2
2	0.0694	0.0694	0.0
3	0.0857	0.0860	+0.4
4	0.1089	0.1087	-0.2
5	0.1156	0.1159	+0.3
6	0.1349	0.1344	-0.4
7	0.1541	0.1536	-0.3
8	0.1782	0.1785	+0.2
9	0.1927	0.1925	-0.1

In order to study this question, a series of titrations of sodium sulfate solutions of varying strengths was carried out. These solutions were prepared from analytical grade salt and standardized gravimetrically either by evaporation and weighing of the residue or by precipitating and weighing as barium sulfate. Throughout the investigation a 0.1 M solution of lead nitrate was used. This solution, also prepared from analytical grade material, was standardized by various methods, both gravimetric and volumetric. The alcohol employed was absolute ethyl alcohol (95 per cent alcohol can also be used with success). The indicator solution was a 1 per cent solution of erythrosin B in water.

The investigation revealed that by adding adequate quantities of alcohol to the sulfate solution accurate results can easily be obtained with final volumes (not counting the alcohol) ranging from 20 to 70 ml. It was found advisable to keep the temperature of the solution below 30° C., in order to avoid a delay of the end point, and to adjust the solution to be titrated carefully so that it reacted just acid towards phenolphthalein. A distinctly basic character caused high results, while a certain degree of acidity (pH = 5) did not produce any harmful effects.

On the basis of these results a number of procedures were tested. In the procedure described below the amount of sulfate to be estimated is limited to approximately 0.19 gram and the final volume of aqueous solution to 70 ml. On exceeding these limits an increasing tendency towards low results is noticeable.

Procedure

MATERIALS AND REAGENTS. A 0.1 M lead nitrate solution, standardized gravimetrically, 1 per cent solution of erythrosin B in water, ethyl alcohol, phenolphthalein solution, and approximately 0.02 N nitric acid.

PROCEDURE. Transfer a 50-ml. sample, containing between 0.05 and 0.19 gram of sulfate, to a 250-ml. Erlenmeyer flask and render just acid to phenolphthalein by means of approximately 0.02 N nitric acid. Add 16 ml. of alcohol and 14 drops of indicator. Mix well, so that the color of the solution is a uniform orange-red. The temperature should not be over 30° C. Run the lead nitrate solution into the flask at a steady dropping rate and with constant swirling until the increasing persistence of the violet color, produced by each drop of standard, indicates the approach of the end point. Continue the titration very slowly and with vigorous agitation until the color of the whole mixture becomes a distinct violet.

Table I shows the results of a number of typical titrations of sodium sulfate solutions carried out according to the above procedure. These indicate that the method is satisfactory, the average relative error being less than 0.3 per cent. The same degree of accuracy was obtained in the titration of

solutions containing potassium sulfate or mixtures of potassium and sodium sulfates.

In order to become well acquainted with the color change that is characteristic for this determination, it is best to titrate a few samples of known sulfate content according to the procedure just described. As soon as the end point has been reached, addition of a drop of lead nitrate solution will no longer cause the appearance of a dark spot on the surface of the mixture.

Successive Titration of Chloride and Sulfate

Owing to the low solubility of lead chloride, especially in an alcoholic medium, all but very small quantities of chloride ions interfere with the operation of the indicator. On the other hand, the presence of considerable quantities of nitrate has no appreciable influence on the end point. This fact suggested the use of silver nitrate for the removal of the chloride ions, thus presenting a method for the successive titration of chloride and sulfate.

A rapid and accurate method for the estimation of chloride, that can be combined with the sulfate determination discussed, is the direct titration with silver nitrate in the presence of fluorescein or dichlorofluorescein as adsorption indicators (1, 3). A preliminary investigation was carried out with solutions containing varying quantities of sodium chloride and sodium sulfate, prepared from analytical grade salts and standardized by the usual gravimetric methods. A 0.1 N solution of silver nitrate, also prepared from analytical grade material and standardized gravimetrically, was used for the various chloride titrations. The indicator solution for the latter was a 0.1 per cent solution of sodium fluoresceinate or sodium dichlorofluoresceinate in water. The other reagents were those employed for the estimation of sulfate in the absence of chloride. The following procedure was used during the investigation:

Transfer a 50-ml. sample, containing between 0.04 and 0.13 gram of chloride and between 0.10 and 0.38 gram of sulfate, to a 250-ml. Erlenmeyer flask and render just acid to phenolphthalein by means of approximately 0.02 N nitric acid. Add 4 to 7 drops of the chloride indicator and titrate with silver nitrate in diffuse light. Run the standard solution into the flask at a steady dropping rate and with constant swirling until the silver chloride starts to flocculate. Continue the titration very slowly and with vigorous agitation until the precipitate turns reddish (end point of the chloride titration). Carefully transfer the contents of the vessel to a 100-ml. volumetric flask, make up to the mark with distilled water, and mix thoroughly. Filter into a dry beaker, after having discarded the first 5 or 10 ml. of the filtrate. Transfer 50 ml. of the clear solution to a 250-ml. Erlenmeyer flask and determine the sulfate according to the directions given above; no further adjustment of the acidity is necessary. Multiply the result of the sulfate titration by two.

TABLE II. SUCCESSIVE TITRATION OF CHLORIDE AND SULFATE

No.	Cl Present Gram	Cl Found Gram	Error %	SO <sub>4</sub> Present Gram	SO <sub>4</sub> Found Gram	Error %
1	0.0464	0.0463	-0.2	0.0982	0.0985	+0.3
2	0.0928	0.0928	0.0	0.0982	0.0979	-0.3
3	0.1392	0.1390	-0.1	0.0982	0.0987	+0.5
4	0.0464	0.0463	-0.2	0.3851	0.3844	-0.2
5	0.0928	0.0930	+0.2	0.3851	0.3840	-0.3
6	0.1392	0.1393	+0.1	0.3851	0.3854	+0.1

Table II shows the results of a number of determinations carried out by this method. The results are satisfactory with regard to both the chloride and sulfate.

Conclusion

From 0.05 to 0.19 gram of sulfate, present in the form of sodium or potassium sulfate, can be estimated rapidly and accurately by means of the procedure described in this paper.



However, the applicability of the erythrosin method is not limited to the conditions set forth in that procedure. One way of extending the scope of the method is based upon the use of standard solutions that have concentrations other than 0.1 *M*. A few determinations carried out with 0.05 *M* and 0.2 *M* lead nitrate showed that with these solutions accurate results can easily be obtained, provided the conditions (quantities of alcohol and indicator) are adjusted adequately. It will be worth while to study the titration with these standards more closely with the purpose of working out analytical procedures for the estimation of amounts of sulfate that are either larger or smaller than those of the above range. Such an extension of the method would also broaden the applicability of the successive determination of chloride and sulfate that has been suggested in this paper. Another

fertile field for further investigation is the replacement of ethyl alcohol by diluents that can be obtained without legal restrictions. Preliminary experiments revealed that both acetone and isopropyl alcohol give satisfactory results, though a somewhat smaller volume is to be used for a given titration as compared to ethyl alcohol.

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## Glass Electrode for Determining Blood pH at 38° C.

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THE procedure for estimating the pH of blood under anaerobic conditions can be facilitated by building a glass electrode into the barrel of a hypodermic syringe. (This hypodermic electrode is now made by Rascher and Betzhold, Inc., Chicago, Ill.) The determination can then be made directly on blood drawn into the syringe within one minute after collection. Any size of barrel may be used, but the 1.5-cc. size has been found most convenient in this laboratory.

The plungers on the market are made of a heat-resisting glass, which will not fuse to Corning 015; therefore, it is necessary to grind a 7.5-cm. (3-inch) length of soft-glass tubing until it fits the barrel to be used. This is easily accomplished with the aid of a turning lathe, using fine silicon carbide powder as an abrasive. One end of this tube is closed off with a thin layer of Corning 015; the maximum thickness of this layer will depend on the measuring instruments employed. One of the author's electrodes, which has a membrane about 0.25 mm. thick, used in conjunction with

a Beckman pH meter, has lasted for more than 5 months, during which time several hundred determinations have been made.

The procedure for determining the pH of blood with this electrode is as follows:

The plunger (after a preliminary soaking in 0.1 *N* hydrochloric acid for 24 hours) is half filled with a solution of 0.1 *N* hydrochloric acid containing a slight excess of quinhydrone, and inserted into the barrel on which the metal clip for holding the plunger in place has been retained. Sufficient neutral sterile isotonic saline solution is then drawn into the syringe with needle attached to fill the air spaces in the needle and between the end of the plunger and the barrel. One drop of saline solution will fill all the air spaces in a well-constructed electrode. The syringe is then held in the hand for a few minutes to raise the temperature of the quinhydrone solution. About 1 cc. of blood is drawn into the syringe, all but about 0.2 cc. of which is immediately expelled, the needle is removed, and the syringe is half immersed in a saturated potassium chloride solution at 38° C. The potassium chloride solution serves as both the salt bridge and the constant-temperature bath as illustrated in Figure 1. A small calomel half-cell is kept in the potassium chloride bath during the procedure. A small thermometer (not shown in diagram) is also kept in the potassium chloride solution. Sufficient warm water at about 40° C. is siphoned to the 50-cc. beaker to keep the contents at 38° C. Placing the 50-cc. beaker in a 100-cc. beaker helps to insulate the contents.

A steady e. m. f. should be obtained within 2 minutes after immersion of the electrode in the potassium chloride solution, the time being dependent on the difference in temperature between the glass electrode and the calomel half-cell. Readings taken more than 5 minutes after withdrawal of the blood from the vein are not to be trusted because of an acid shift which becomes appreciable at that time. No acid shift is observed in blood within the first 3 minutes if the temperature is carefully controlled. Clotting does not have a measurable effect on the observed pH (1).

If one is careful to check each electrode with standardized buffers before and after each series of determinations, an accuracy of better than 0.02 pH unit may be obtained.

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RECEIVED July 6, 1938. Demonstrated at Baltimore meeting of American Society of Biological Chemists, April, 1938.

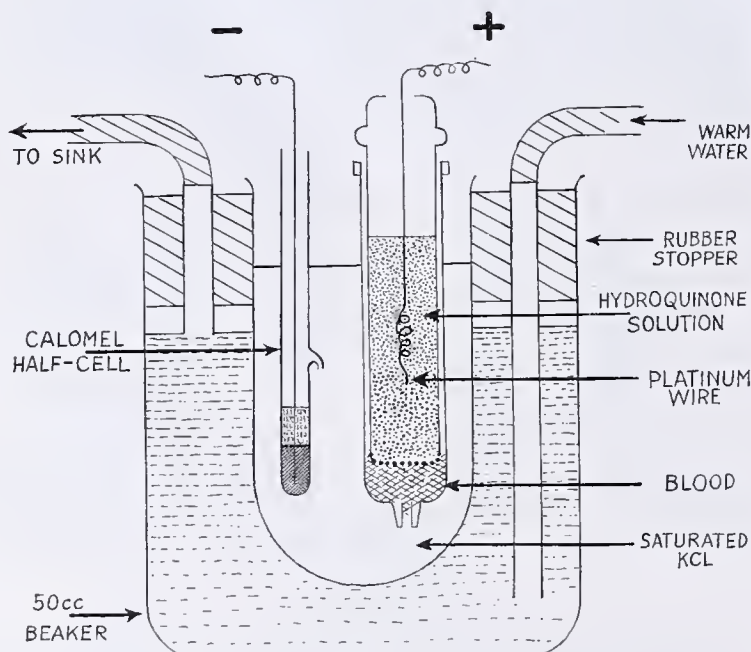


FIGURE 1. DIAGRAM OF APPARATUS  
Corning 015 gl ss indicated by dotted line

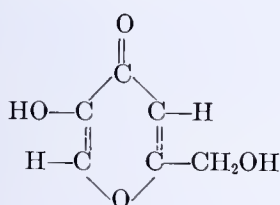


# Copper Precipitation Method for Kojic Acid Determination

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KOJIC acid, 2-hydroxymethyl-5-hydroxy- $\gamma$ -pyrone, may be produced in quantity by the proper fermentation of glucose and xylose solutions with members of the *Aspergillus flavus-oryzae* groups of molds. Interest in it has been shown because of its possible utilization for industrial purposes. Its accepted structural formula is:



Several methods have been employed for its quantitative estimation, the merits of which depend upon the quantity of the compound present and the nature of the investigation. Tamiya (9) and Corbellini and Gregorini (6) used a colorimetric method based upon the intense red coloration produced when kojic acid is treated with ferric chloride. Challenger, Klein, and Walker (5) repeatedly extracted culture media and washings with ether and weighed the product. Birkinshaw and Raistrick (4) developed a method of oxidizing kojic acid with an alkaline solution of iodine which is suitable in the presence of glucose, provided the analysis for glucose is made independently. In the absence of other acids, kojic acid may be determined with fair accuracy by titrating its solutions with dilute alkali, using alizarin orange R (8) or phenolphthalein (to full red color over a source of diffused light) (3) as indicators.

TABLE I. EFFECT OF VARIATION OF COPPER ACETATE CONCENTRATION

0.72 N Copper Acetate Cc.	No Alkali			Neutral			Equivalent Alkali		
	Copper kojate Gram	CuO %	Fil- trate pH	Copper kojate Gram	CuO %	Fil- trate pH	Copper kojate Gram	CuO %	Fil- trate pH
2	0.1715	22.9	4.2	0.1740	22.7	5.9	0.1742	22.9	6.4
5	0.1647	22.8	5.0	0.1667	23.0	6.0	0.1706	23.8	6.0
10	0.1564	22.9	5.2	0.1566	23.6	5.7	0.1567	23.3	5.8
15	0.1459	23.3	5.2	0.1471	23.2	5.6	0.1467	23.0	5.6
20	0.1345	23.3	5.2	0.1353	23.1	5.5	0.1372	23.4	5.5
25	0.1175	23.2	5.2	0.1266	23.4	5.4	0.1275	23.4	5.5

For most purposes, the most convenient and accurate method is to precipitate the kojic acid from its neutralized solutions with dilute copper acetate and weigh the dried copper kojate. May, Moyer, Wells, and Herrick (8) used this method in their experiments; their assumption that the copper salt was the half-hydrate,  $(C_6H_5O_4)_2Cu \cdot \frac{1}{2}H_2O$ , was based upon their value of 22.40 per cent of copper oxide in the salt. Maurer (7) found 22.12 per cent of copper oxide which is approximately midway between the values corresponding to the half-hydrate and monohydrate. The molecular formulas,  $(C_6H_5O_4)_2Cu$  and  $(C_6H_5O_4)_2Cu \cdot H_2O$ , have been reported by Yabuta (11) and Traetta-Mosca (10), respectively.

For several years, the author and others (1, 2, 3) have found it satisfactory to assume that copper kojate precipi-

tates as the half-hydrate. In making the determination, no predetermined quantity of the copper acetate precipitant was added although it was common practice to add what was believed to be a small excess. More recent experience with the method, especially in the analysis of certain derivatives of kojic acid which retain the acidic character of the parent compound (1), gave the impression that the excess of precipitant is an important factor in the accuracy of the method. This raised a question as to the validity of the assumption of the half-hydrate. It was thought desirable, therefore, to investigate this factor as well as other conditions surrounding the precipitation of copper kojate and the treatment of the precipitate before weighing.

## Experimental

PRECIPITATION AND COPPER OXIDE DETERMINATIONS. Unless otherwise stated, all precipitations were made in quadruplicate from solutions having a total volume of approximately 75 cc. and the data given are averages. The precipitates were filtered and washed in Gooch crucibles prepared with all the care required by the usual quantitative procedure. The accuracy of the work with Gooch crucibles was checked against that of fritted glass crucibles of the Gooch type with respect to both the precipitates themselves and the copper oxide derived from them. The copper oxide percentage was determined by igniting the precipitates to constant weight at ca. 525° C. Copper oxide percentages determined by ignition agreed closely with those determined by iodometry.

KOJIC ACID. The kojic acid used in these experiments was carefully purified by repeated crystallizations from water and alcohol, followed by extraction with chloroform. The chloroform-extracted kojic acid had a melting point of 152–3° C. In all cases, 10-cc. aliquots of 0.1 N kojic acid were precipitated and the weights of copper kojate were reported on that basis. The calculated weight of anhydrous copper kojate derivable from this quantity of kojic acid is 0.1729 gram; its calculated copper oxide percentage is 23.01 per cent.

SODIUM HYDROXIDE. It was necessary to titrate the solutions with standard alkali before precipitation to bring the pH within the required range and, more especially, to ascertain the maximum kojic acid concentration so that the proper excess of precipitant could be added. The 0.1 N sodium hydroxide solution used was freshly prepared, since solutions which have stood indefinitely give high results due to silicates dissolved from glass containers.

PRECIPITANT. The cupric salt to be used as the precipitant must be the salt of a weak acid such as copper acetate. Copper sulfate, for instance, lowers the pH prevailing at the time of precipitation, to the extent that an appreciable fraction of the copper kojate remains in solution. The standard stock solutions of copper acetate were filtered before using to avoid the addition of any basic salt which may have formed on standing. Five cubic centimeters of the precipitant (0.3 or 0.72 N copper acetate) were added in each experiment except those in which the concentration of copper acetate was varied.

EFFECT OF VARIATION OF COPPER ACETATE. The concentration of copper acetate was varied in solutions to which no alkali had been added, in those which had been made neutral with alkali (pink color of phenolphthalein), and in those to which the equivalent of alkali (full red color of phenolphthalein) had been added. The results of this variation are presented in Table I.

EFFECT OF BUFFERING WITH SODIUM ACETATE. For experiments involving the variation of sodium acetate concentrations, the two smaller copper acetate concentrations of Table I—2 cc. (ca. 5 cc. of 0.3 N) and 5 cc. of 0.72 N—were chosen; nothing was to be gained by using still greater concentrations. Sodium acetate solutions (10-cc. portions, or the equivalent) with the approximate normalities 0.1, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 6.0, and 8.0 were added to the solutions to be buffered after they had been titrated with 0.1 N sodium hydroxide to the pink color of phenolphthalein. pH measurements were made with a Coleman pH electrometer. The results are given in Table II.



**SOLUBILITY OF COPPER KOJATE IN WATER.** A quantity of copper kojate was prepared by adding a slight excess of copper acetate to a solution of kojic acid at a pH of about 4.0. The dry salt contained 22.8 per cent of copper oxide by ignition and by iodometry. Samples of this copper kojate were stirred with distilled water for 12 hours and the resulting suspensions filtered, dried, and weighed. There was no change in the weights of the samples nor had sufficient salt dissolved for the filtrate to give a perceptible color with ferric chloride (this test for kojic acid is sensitive to 1/200,000) or with ammonium hydroxide.

TABLE II. EFFECT OF BUFFERING WITH SODIUM ACETATE

Normality of Sodium Acetate	5 cc. of 0.3 N Copper Acetate			5 cc. of 0.72 N Copper Acetate		
	Copper kojate Gram	CuO %	Filtrate pH	Copper kojate Gram	CuO %	Filtrate pH
0.1	0.1739	22.9	5.9	0.1682	23.3	5.8
0.5	0.1742	23.0	6.3	0.1684	23.3	6.1
1.0	0.1742	22.7	6.6	0.1690	23.5	6.3
1.5	0.1742	22.8	6.7	0.1742	24.4	6.4
2.0	0.1738	22.7	6.8	0.1744	24.4	6.5
3.0	0.1742	22.8	7.0	0.1800	25.6	6.7
4.0	0.1740	22.8	7.2	0.1802	25.9	6.9
6.0	0.1739	22.7	7.4	0.1822	25.9	7.0
8.0	0.1743	22.8	7.6	0.1826	26.0	7.2

**PRECIPITATION PERIOD.** In order to determine the time required for complete precipitation of copper kojate without basic salt formation, kojic acid solutions, to which had been added the equivalent of 0.1 N sodium hydroxide, were precipitated by the addition of 5 cc. of 0.3 N copper acetate. The precipitates were filtered off at intervals, then dried, and weighed. The results are shown in Table III.

TABLE III. PRECIPITATION PERIOD

Hours	Copper Kojate Gram
2	0.1570
4	0.1634
6	0.1662
8	0.1669
24	0.1710
36	0.1732
48	0.1740
60	0.1741
72	0.1738

**DRYING OF PRECIPITATES.** Ten cubic centimeters of 0.1 N kojic acid should give 0.1729 gram of copper kojate on the basis of the anhydrous salt. Drying *in vacuo* over calcium chloride gave constant weights which averaged approximately 0.1740 gram. Drying in an air oven from 6 to 8 hours at 100° C. also gave weights which averaged approximately 0.1740 gram but with slightly more variation between individual weights. After drying in an air oven for 16 to 24 hours at 100° C. the weights averaged 0.1728 gram but the individual differences were still greater. Continued heating in an air oven at 100° C. or above showed that slow decomposition of the copper kojate occurs and that the resulting weights depend upon the temperature recorded by the oven and the period of heating. However, prolonged drying *in vacuo* at 100° C. gave weights which averaged 0.1736 gram. Heating later at 105° C. *in vacuo* showed no further change in the weights. Twelve samples, from which this average was calculated, weighed 0.1737, 0.1733, 0.1736, 0.1738, 0.1735, 0.1738, 0.1735, 0.1737, 0.1734, 0.1740, 0.1736, and 0.1733 gram, with a spread of 0.0007 gram. This serves to illustrate the distribution and maximum spread of weights which may be expected when the samples are dried without decomposition. Higher temperatures *in vacuo* which might have given constant weights corresponding to the anhydrous salt (0.1729 gram) were not used. If this could be done without decomposition, it might be expected that individual weights would check even more closely.

Copper kojate samples which have been dried *in vacuo* or in an air oven exhibit no tendency to absorb moisture while standing in air for 24 hours.

### Discussion

For an adequate test of the suitability of this method for kojic acid determination, it is regarded as sufficient to establish conditions which permit the complete precipitation of copper kojate without basic salt formation. This information would also make it possible to estimate the extent of hydration of copper kojate.

Copper kojate is practically insoluble in distilled water and in relatively large concentrations of sodium acetate (Table II), since increasing quantities of sodium acetate have no effect on the quantity of copper kojate obtained from 10 cc. of 0.1 N kojic acid. However, copper acetate does exert a solvent action on copper kojate proportional to the excess of copper acetate in solution (Table I). Therefore, so far as these experiments are concerned, there is complete precipitation of kojic acid as copper kojate from solutions containing approximately 0.142 gram of kojic acid in 75 cc. and no more than 50 per cent excess of copper acetate.

An inspection of Table II will show also that, in experiments in which 10 cc. of 0.1 N kojic acid were precipitated by the addition of 5 cc. of 0.3 N copper acetate, the weights of the precipitates as well as the copper oxide percentages are constant within the pH range of 6.0 to 7.5. However, if similar precipitations are made with 5 cc. of 0.72 N copper acetate, both the weights of the precipitates and the copper oxide percentages increase with the pH. The conclusion follows, therefore, that the precipitation of weights of copper kojate greater than approximately 0.1740 gram from 10 cc. of 0.1 N kojic acid is due to the formation of basic salts of kojic or acetic acids.

TABLE IV. REPORTED FORMS OF COPPER KOJATE

Form of Copper Kojate	Copper Kojate Gram	Copper Oxide %
$(C_6H_5O_4)_2Cu$	0.1729	23.01
$(C_6H_5O_4)_2Cu \cdot \frac{1}{2}H_2O$	0.1774	22.43
$(C_6H_5O_4)_2Cu \cdot H_2O$	0.1819	21.87

Mention was made above of the different forms of copper kojate which have been reported. Which of these forms is the true one may be determined by the maximum weight of normal copper kojate obtainable from a given quantity of kojic acid. For purposes of comparison, the calculated weights of the different forms of copper kojate and corresponding copper oxide percentages equivalent to 10 cc. of 0.1 N kojic acid are given in Table IV. In every instance where weights of the order of 0.1774 or 0.1819 gram were obtained, there was evidence of basic salt formation. The experimental values, 0.1740 gram of copper kojate and 22.8 per cent of copper oxide, agree more closely with corresponding values of anhydrous copper kojate than with those of the half-hydrate or monohydrate. When it is recalled that copper kojate exhibits no tendency to form hydrates at room temperature and, also, that prolonged drying *in vacuo* at 100° to 105° C. reduces slightly the average copper kojate weights without decomposition, it appears a justifiable conclusion that, under the proper conditions, kojic acid is precipitated as anhydrous copper kojate containing a small quantity of strongly adsorbed water.

### Summary

The copper precipitation method, when properly carried out, is an accurate method for the estimation of kojic acid. The solutions to be analyzed should be titrated first with standard alkali to the full red color of phenolphthalein, diluted until the kojic acid concentration is approximately 0.142 gram in 70 cc., and dilute copper acetate added in an excess which does not exceed 50 per cent of the amount determined by titration. At least 48 hours are required for complete precipitation, after which the precipitates are removed by filtration, washed, dried, and weighed as anhydrous copper kojate,  $(C_6H_5O_4)_2Cu$ . The precipitates may be dried without decomposition *in vacuo* over calcium chloride or in a vacuum oven at 100° to 105° C. The pH of the solution is not critical; it is sufficient to keep the filtrates within the pH range of 6.0 to 7.5.



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# Determination of Active Ingredients and Fatty Matter in Surface-Active Agents

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THE discovery that a sulfo group on a primary carbon of an aliphatic chain of the proper molecular weight, which may or may not be condensed with an aryl group, produces compounds that possess sudsing and scouring properties has led to a flood of patents on synthetic detergents. A good many such compounds are now on the market and their applications in the industries are already extensive and increasing. The synthetic surface-active agents are preferred to soap in numerous industrial operations, particularly in those processes where hard water is used or where the alkalinity due to the hydrolysis of soap is objectionable. Practically all the products available commercially contain considerable quantities of Glauber's salt, because of the process of manufacture or admixture where the product is marketed in the form of a powder. They are usually sold on an "as is" or performance basis, hardly ever on their content of active ingredients. No reliable method for estimating the effective ingredients in such products seems to have been described in the literature.

A method is here outlined for the determination of active ingredients in true sulfonic compounds and in sulfuric acid esters. It is applicable to such products as the sulfated fatty alcohols, sulfonated fatty acid amides or esters, sulfonated alkyl naphthalenes, sulfonated mineral oils, etc., and to the older type of sulfonated oils, such as sulfated castor or olive oil, sulfated oleic acid, sulfated tallow, etc. In the case of the latter type, the trade is accustomed to evaluate a given product by its content of fatty matter. The new method does not determine the fatty matter directly but it may readily be calculated from the active ingredients. The new method is not so convenient nor rapid, but the results are believed to be more accurate than those obtained by the usual method of acid hydrolysis and extraction; the fatty matter during hydrolysis may undergo various changes, such as loss of glycerol, formation of lactones and lactides, polymerization, re-esterification, etc., all of which affect the final weight of the fatty matter in both directions, the net effect depending upon the conditions of the hydrolysis and the nature of the sample. The new method consists essentially of extracting the active ingredients with solvents over a concentrated salt solution, evaporating the solvent, heating the residue to constant weight, and determining the loss in weight upon ashing the residue.

## Procedure

**RESIDUE BEFORE ASHING.** The combined solvent layers from the determination of organically combined sulfuric anhydride by the ammonia method (1) are transferred to a tared 150-ml. beaker. The solvent is evaporated and the residue heated at 105° to 110° C. to constant weight.

In the case of sulfuric acid esters it is necessary to stabilize the oil with alkali before heating; otherwise the residue turns black because of decomposition. For ordinary sulfated oils, the addition of 2 ml. of 0.5 N alcoholic potash is sufficient to effect stabilization; with highly sulfated oils, double that quantity is required. The first sign of decomposition is when the residue begins to turn red, owing to the effect of the liberated sulfuric acid on the methyl orange present in the oil. With sulfonic compounds the use of alkali is not required.

A more rapid means of reaching constant weight is to heat the beaker, after practically all the solvent has been evaporated on a steam bath, in an oil bath at 135° C. with stirring for 15- to 20-minute periods. In that event the beaker should be provided with a tared glass rod. If the residue is very viscous or solid, an amount of oleic acid (previously heated for 10 minutes at 150° C.) approximately equal to the weight of the residue is added. This serves to liquefy the residue and hasten evaporation of the solvent.

**RESIDUE AFTER ASHING.** The residue is quantitatively transferred to a tared crucible, preferably platinum. Traces of the residue in the beaker are wiped clean with ashless filter paper moistened with solvents and finally with hot water, and the several pieces of filter paper are added to the crucible. The contents of the crucible are burned off and finally ignited until practically all the carbon is consumed; if necessary, the residue may be treated several times with small quantities of 30 per cent hydrogen peroxide. The ash is then treated with 2 ml. of concentrated sulfuric acid, the acid is evaporated, and the residue is ignited strongly until the weight is constant, preferably with a blast burner.

**TOTAL ACTIVE INGREDIENTS.** The difference in weight before and after ashing represents the loss of organic matter plus sulfur trioxide in the case of ester compounds or sulfur dioxide in the case of sulfonic compounds, in accordance with the following reactions:

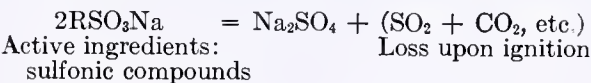
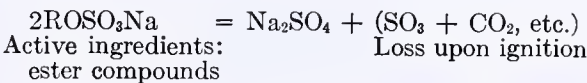




TABLE I. TOTAL FATTY MATTER AND TOTAL ACTIVE INGREDIENTS IN SULFURIC ACID ESTERS

	Total Fatty Matter— New method			Matter— Acid-decomposition method			Total Active Ingredients, New Method		
	I	II	Av.	I	II	Av.	I	II	Av.
	%	%	%	%	%	%	%	%	%
Sulfated oleic acid	61.6	61.8	61.7	61.5	61.4	61.5	66.5	66.8	66.7
Sulfated castor oil	60.6	60.3	60.5	60.9	60.5	60.7	65.6	65.3	65.5
Sulfated tallow	83.4	83.1	83.3	82.9	83.0	83.0	86.6	86.3	86.5
Sulfated blended oil <sup>a</sup>	76.9	76.8	76.9	76.4	76.7	76.6	80.3	80.2	80.3
Highly sulfated castor oil	31.7	31.3	31.5	31.6	31.4	31.5	40.2	39.8	40.0
Sulfated fatty alcohol <sup>b</sup>	23.5	23.6	23.6	23.5	23.8	23.7	31.4	31.5	31.5

<sup>a</sup> Used in spinning rayon.<sup>b</sup> Oleyl and cetyl alcohols.

TABLE II. LOSS UPON IGNITION OF PURIFIED SAMPLES OF SULFONIC COMPOUNDS AND TOTAL ACTIVE INGREDIENTS

	Loss upon Ignition, Purified Sample		Total Active Ingredients, Sample "As Is,"		
	New method, av.	Direct method, ignition, av.	New Method		
	%	%	I	II	Av.
Fatty acid amide sodium sulfonate	85.8	85.0	27.6	27.3	27.5
Alkyl naphthalene sodium sulfonate	78.4	78.7	64.9	64.6	64.8
Alkyl aryl sodium sulfonate	80.2	79.9	34.6	34.8	34.7

Sulfuric acid is added to the ash in order to convert into sulfates the sulfides and sulfites which are formed upon ignition. The above reactions show that the total active ingredients for both types of compounds, represented by the right-hand side of the equations, are equal to the "loss upon ignition" plus one-half of the combined sulfuric anhydride as sodium sulfate. Hence, the total active ingredients may be calculated from the combined sulfuric anhydride and "loss upon ignition" (corrected as shown below) as follows:

$$\begin{aligned}
 & 1. \text{ Total active ingredients, per cent} \\
 & = \frac{100 \times \text{loss upon ignition (corrected)}}{\text{weight of sample}} + \\
 & \quad \frac{\text{Na}_2\text{SO}_4}{2\text{SO}_3} \times \% \text{ combined SO}_3 \\
 & = 0.8875 \times \% \text{ combined SO}_3 + 100 \times \frac{\text{loss upon ignition (corrected)}}{\text{weight of sample}}
 \end{aligned}$$

Where alcoholic potassium hydroxide had been added, the loss in weight upon ignition is too high by an amount equal to (K - H) and too low by the corresponding amount of potassium sulfate. The corrections for these two items are made as follows:

Correction for (K - H), in grams

$$\begin{aligned}
 & = - \left[ \frac{(K - H)}{\text{KOH}} \times \frac{\text{mg. of KOH added}}{1,000} \right] \\
 & = -(0.0006774 \times \text{mg. of KOH added})
 \end{aligned}$$

Correction for K<sub>2</sub>SO<sub>4</sub>, in grams

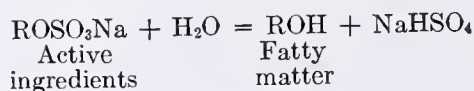
$$\begin{aligned}
 & = \frac{\text{K}_2\text{SO}_4}{2\text{KOH}} \times \frac{\text{mg. of KOH added}}{1,000} \\
 & = 0.001552 \times \text{mg. of KOH added}
 \end{aligned}$$

Total correction, grams

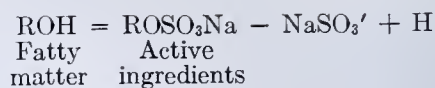
$$\begin{aligned}
 & = -0.0006774 \times \text{mg. of KOH added} + 0.001552 \times \text{mg. of KOH added} \\
 & = +0.0008746 \times \text{mg. of KOH added}
 \end{aligned}$$

### Total Fatty Matter

In calculating the fatty matter from the active ingredients in samples of sulfuric acid esters, it may be assumed that the latter upon hydrolysis yield a hydroxy group for every combined sulfuric anhydride split off, as follows:



Hence



Consequently the fatty matter is given by the following formula:

$$\begin{aligned}
 & 2. \text{ Fatty matter, per cent} \\
 & = \% \text{ active ingredients} - \frac{(\text{NaSO}_3' - \text{H})}{\text{SO}_3} \times \% \\
 & \quad \text{combined SO}_3 \\
 & = \% \text{ active ingredients} - 1.275 \times \% \text{ combined SO}_3 \\
 & = 100 \times \frac{\text{loss upon ignition (corrected)}}{\text{weight of sample}} - \\
 & \quad 0.3875 \times \% \text{ combined SO}_3
 \end{aligned}$$

From the last formula, it will be noted that an error of 1 per cent in the combined sulfur trioxide determination will affect the fatty matter by less than 0.4 per cent.

### Experimental

**SULFURIC ACID ESTERS.** The fatty matter in sulfuric acid esters by the new method compared with the fatty matter obtained by the acid-decomposition method is given in Table I, in which also the total active ingredients are listed.

**SULFONIC ACIDS.** A number of different true sulfonic compounds were dissolved in a small quantity of water and acidified with sulfuric acid, and the solutions were evaporated to dryness. The residues were then dissolved in hot alcohol, filtered, and again evaporated to constant weights. A portion of each residue was then extracted according to the new method and the loss in weight upon ashing was determined. This was compared with the loss in weight upon direct ashing of the rest of the residue. The results are given in Table II which also includes the total active ingredients contained in the original samples.

It is evident that in the case of sulfonic compounds the loss of organic matter plus volatile sulfur (upon which the new method for active ingredients depends) may be determined directly by ashing the original sample, provided the moisture in the sample is known and there is no other salt present than sodium sulfate. This is also true of the sulfuric acid esters, but, in addition to the above, it is necessary to know the alkalinity of the sample and whether or not the alkali is sodium or potassium.

### Summary

An accurate method for the determination of active ingredients in sulfuric acid esters and sulfonic compounds is outlined. This depends upon extracting the active ingredients, which may be contaminated with sodium sulfate but no other salts, and determining the loss in weight upon ignition. A method is also given for the determination of fatty matter in sulfuric acid esters, provided the organically combined sulfuric anhydride is known.

### Acknowledgment

The writer is greatly indebted to Virginia Raison of this laboratory for assistance with the analytical work and to H. W. Elley, associate chemical director of E. I. du Pont de Nemours & Co., Inc., for a sample of 2-naphthalenesulfonic acid.

### Literature Cited

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# Viscometer for Routine Determination of Proteolytic Activity of Malts

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The apparatus is very simple to construct and use. One temperature (40° C.) is used for standardization, extraction, digestion, and viscosity determinations. Better timing visibility is obtained. Absolutely constant volume is assured during a series of readings.

No aliquot parts are taken from a changing substrate after digestion is started, no transfer of hot liquids to the viscometer is required as specified for the gelatin industry, there is no clogging due to evaporation at the tip, and intermediate cleaning is unnecessary between samples in a run.

The simple design of the viscometer permits three simultaneous runs in less than 2 hours. The filled viscometer can be inverted at once, making accurate extrapolations possible. No buffering is required. The proteolytic activity value increases with the amount of enzyme. One minute of digestion corresponds to one point of activity.

THE present paper is a continuation of work done at Marquette University on various materials containing proteolytic enzymes, as a result of which a paper was published on the use of gelatin as a substrate for measuring enzyme activity of commercial bating preparations (6). In this work the modified Bloom viscometer was used as standardized for the glue and gelatin industry.

As an outgrowth of this work, the viscometers as shown in Figure 1 were developed, for the purpose of eliminating as many sources of error as possible and making the operation extremely simple. During these experiments Ehrnst suggested that the viscometer could be nicely adapted to the determination of the proteolytic activity of malt.

Robert Wahl, basing his work on research done by Nilson (4), found that malt infusions prepared with water acidified with a small amount of bacterial lactic acid (0.1 to 2 per cent) would liquefy gelatin to a greater degree than did aqueous extracts. Commercial lactic acid and inorganic acids yielded no increase in proteolytic activity. Wahl used diluted solutions of pepsin (1 to 10,000 strength) as a standard for comparison, allowing them to react on the gelatin under the same conditions as the malt infusions. Later he modified this method of comparison (12), and more recently A. Wahl has introduced papain as a standard for comparison (10).

The authors' method of extraction followed the procedure of Wahl (12) except that no lactic acid was used. As an indication of proteolytic activity, the viscosity of gelatin was used instead of setting time. In 1937 Laufer (3) determined the proteolytic activity of malt by means of a gelatin vis-

cosity method and an Ostwald pipet. Although the viscosity of gelatin has often been used to estimate proteolytic activity (1, 5, 6, 13), Wahl (12) and Laufer (3) seem to have been the first to adapt these methods to malt.

An extensive bibliography on the determination of proteolytic activity in general is given by Orthmann, Surak, and Koch (6), and with the paper by Laufer which brings the literature on malt up to date (3) furnishes a rather complete survey of the literature.

The purpose of the present investigation has been to adapt the new viscometer to the routine determination of the proteolytic activity of malts.

## Need for Simple Method of Determining Proteolytic Activity of Malts

The presence of nitrogenous or albuminoid substances has considerable effect on the finished product in regard to clarity (7), chill-proofing (7), body, and flavor (11). Because many of the substances which are added to beers to prevent haziness when chilled are actually enzymes, a knowledge of the proteolytic activity of a malt is important to the maltster as well as to the brewer. It is possible to determine the



FIGURE 1. VISCOMETERS

Left. With rubber stopper  
Right. All-glass type



proteolytic strength of malt and then to arrive at a clue as to its processing.

No method for determining proteolytic activity up to the present time has been simple or rapid enough to be generally adopted by malt or brewing laboratories. The viscometer presented herewith is as simple to operate as the ordinary kitchen egg-timer and the apparatus can be constructed in any laboratory without the aid of a glass blower. The determination is designed to meet the needs of a malting or brewing laboratory.

The method is based on the well-known principle that the viscosity of gelatin decreases as it is attacked by a proteolytic enzyme (1, 3, 5, 6, 13).

The viscometer consists of two Erlenmeyer flasks connected at the necks with a capillary tube. An air tube is provided so that no pressure will be built up in either flask as the viscometer is tilted back and forth. In the type made up with rubber stoppers the air tube is inside the flasks. If determinations are to be made regularly, the all-glass type can be made (Figure 1, right). In either case, the capillary should have a bore of about 1.5 mm. and be from 2.5 to 3.7 cm. in length. At room temperature 50 cc. of water should go through the capillary in the neighborhood of 35 or 36 seconds. This can be ascertained in advance and a different length or a different bore chosen, so that the finished viscometer will have a convenient and accurate time of flow.

The standardization is made at the same temperature as the experimental viscosity determinations and all factors such as volume, temperature, and pressure must necessarily

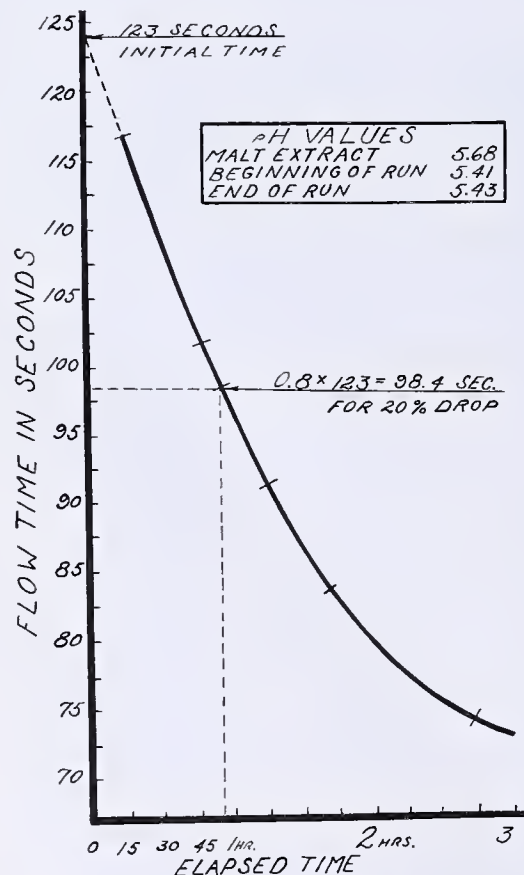


FIGURE 2. A TYPICAL RUN, MALT 10  
pH at Beginning of Run, 5.41; at End of Run, 5.43.  
pH of Malt, 5.68. Viscometer 4

Run	Elapsed Time Min.	Flow Time Sec.
1	15	116.8
2	45	101.7
3	75	91.4
4	105	84.2
5	135	78.4
6	165	74.5

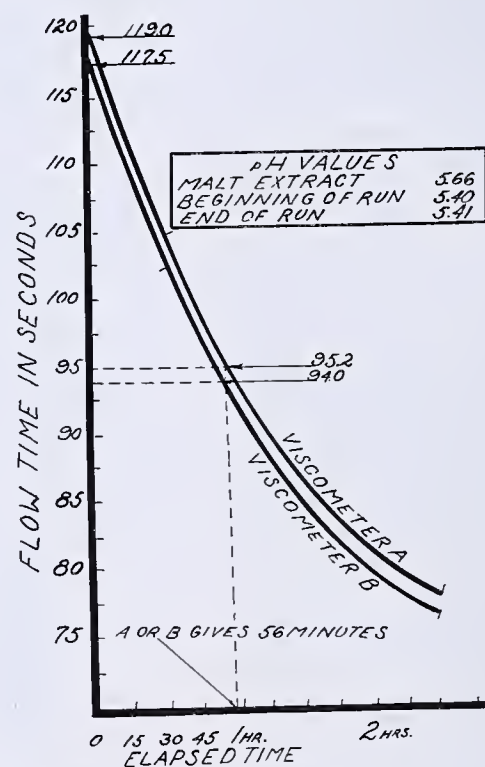


FIGURE 3. VISCOSITY DROP WITH  
SIMILAR VISCOMETERS

pH at Beginning, 5.40; at End, 5.41. pH of  
Malt, 5.66

Run	Elapsed Time Min.	Flow Time Sec.
Viscometer A		
1	0	119.0
2	15	112.0
3	30	104.8
4	45	98.0
5	75	90.5
6	105	84.4
7	135	79.4
Viscometer B		
1	0	117.5
2	15	109.6
3	30	102.2
4	45	97.2
5	75	89.8
6	105	82.5
7	135	78.0

remain constant throughout the entire series of determinations. If a number of viscometers are made from one piece of capillary tubing, their flow times will be found to be so close that check results or direct comparisons can be made. On the other hand, if the viscometers are not duplicated, the standardization takes care of all variations. Different laboratories can compare figures for proteolytic activities or the figures for proteolytic activity here given can be used as a standard, if reasonable care is taken to select a gelatin of approximately the same characteristics. Proteolytic values of several laboratories have been found to compare nicely, even with operators of very little training.

## Comparison of the Proteolytic Activity of Malts

**PREPARATION OF 10 PER CENT GELATIN SOLUTION.** In the present experimental work a new gelatin solution was made for each determination. If extreme accuracy is not necessary, larger quantities can be made up and kept in the ice box for several days or even longer (13).

In order to prepare 250 cc. of 10 per cent gelatin, 25 grams of isinglass or other gelatin of good quality are sprinkled on top of about 125 cc. of distilled water at room temperature. The gelatin is stirred well and allowed to stand for a half hour. The beaker is now immersed in water held at a temperature of 60° to 65° C. and the gelatin stirred until dissolved. The contents of the beaker are transferred to a 250-cc. volumetric flask and the beaker is rinsed repeatedly with warm water. A 10 per cent solution is obtained by making up to the mark.

**PREPARATION OF MALT INFUSION CONTAINING PROTEOLYTIC ENZYME.** A quantity of malt is finely ground in a Miag-Seck mill, 20 grams are transferred to a 250-cc. beaker, 100 cc. of distilled water at 40° C. are added, and the infusion is well stirred and placed in a water bath at 40° C. The infusion is stirred frequently for 0.5 hour, and then filtered. Thirty-five or 40 cc. are now placed in the water bath at 40° C. and allowed to stand for about 8 minutes. The following steps indicate the method of combining the malt infusion solution and the gelatin solution:

1. Twenty-five cubic centimeters of malt infusion at 40° C. are added to 50 cc. of 10 per cent gelatin solution at 40° C. and the time is noted. This is the so-called "zero" or initial time.

2. Fifty cubic centimeters of this infusion-gelatin mixture are placed in the viscometer (attenuated at 40° C.) and a determination is made in 15 minutes from the zero time. The first run may be made sooner if desired. [The amount taken is actually 50 cc. plus the 1 or 2 cc. (accurately determined for each viscometer) trapped on the two sides of the viscometer because of the slight extension of the capillary. This extension of the capillary causes the gelatin to run freely from the tip without touching the sides of the Erlenmeyer.]

3. Subsequent determinations may be made every 15 minutes thereafter.

4. In practically all cases sufficient action has taken place in a 2-hour period to give a good graphic history.

Obviously, since all solutions are at 40° C. prior to and after mixing, temperature changes are held to an absolute minimum. A single temperature for extraction and di-





GROWING FLOOR, SHOWING MECHANISM FOR TURNING GRAIN

gestion has proved very desirable, as it prevents error due to variation in temperature adjustment. The temperature should be high enough to hasten the action of the enzyme but should not exceed the temperature at which the enzyme is stable. The authors' experience with many hundreds of runs has placed this at 40° C.

A TYPICAL RUN. Although viscosities are best reported as kinematic viscosities, as outlined below, they can also be reported in terms of seconds for the 50-cc. flow through the viscometer. If viscometers of practically the same characteristics are made, the proteolytic activity of a series of enzymes can readily be compared without need for any standardization. Standardization and expression of results in kinematic viscosity are necessary only when using dissimilar viscometers, or when comparisons are to be made between different laboratories.

Figure 2 shows a typical run for a malt. Since the solution and viscometer are at 40° C., time of flow can be measured almost immediately after the viscometer has been put into the bath. As time elapses, the proteolytic enzymes of the malt break down the gelatin and its viscosity decreases (Figure 2). The dotted lines indicate the number of minutes required for a 20 per cent drop in viscosity. This is the number of minutes used to indicate the proteolytic strength of the malt in question.

Naturally the shorter the time taken to produce this 20 per cent drop in viscosity, the stronger the malt in proteolytic activity.

As indicated in Figure 2 (malt 10), initial time is obtained by extrapolating the graph. Numerous experiments have shown that this gives the same time of flow as a blank of gelatin and malt infusion boiled to kill the enzymes and therefore, in experimental runs, a blank determination is not necessary. The initial time gives a flow of 123 seconds, which multiplied by 0.8 gives 98.4 seconds as the time when the viscosity has decreased 20 per cent. Referring to the elapsed time on the horizontal axis, it required 55 minutes for this particular malt to produce a 20 per cent drop in viscosity.

Such figures will enable any purchaser of malts to arrange any number of samples in the order of their proteolytic activity.

MALT VALUES WITH LIKE VISCOMETERS. That the same lengths of capillary cut from the same piece will give very similar viscometers, and that these viscometers will give the same elapsed time for a 20 per cent drop in viscosity, are clearly indicated in Figure 3. The upper curve represents malt 8 in viscometer A, while the lower curve represents the same malt in viscometer B. In either case it required 56 minutes to produce a 20 per cent drop in viscosity.

EFFECT OF PROCESSING. In Figure 4 the curves for malts 2 and 3 are very similar. These malts were processed alike although they came from different sources. Malt 1 was made by a different process and has an entirely different slope to the curve. This set of curves shows that the graphic history of the digestion gives valuable information in addition to giving the minutes necessary for a 20 per cent drop.

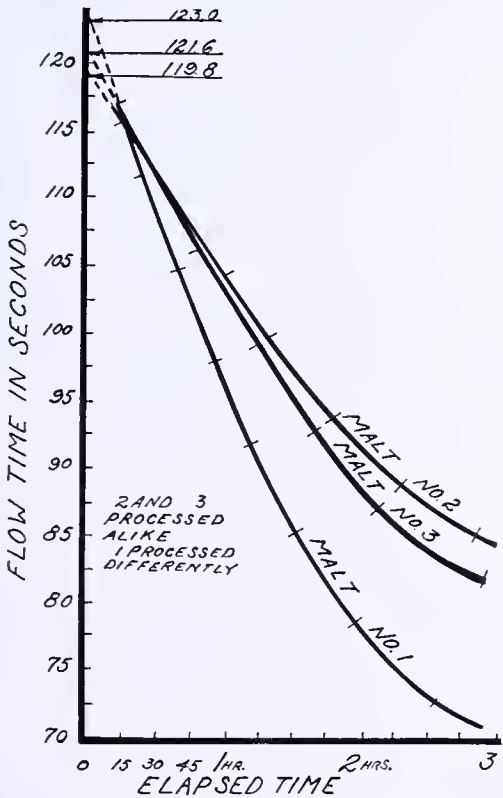


FIGURE 4. EFFECT OF DIFFERENCE IN PROCESSING  
(See tables, right)

Experimental Data

The maximum proteolytic activity of malt lies between pH of 5 and 6 (3, 13).

In order to test the viscometer as to sensitivity, accuracy, and adaptability (it has been used for testing various gelatins

pH at Beginning, 5.36; at End, 5.12. Malt 1.		
Run	Elapsed Time Min.	Flow Time Sec.
Viscometer 3		
1	15	114.7
2	45	104.8
3	75	90.0
4	105	82.3
5	135	75.0
6	165	72.0
pH at Beginning, 5.39; at End, 5.38 Malt 2.		
Viscometer 2		
1	15	115.2
2	45	108.1
3	75	102.0
4	105	95.8
5	135	89.9
6	165	87.0
pH at Beginning, 5.41; at End, 5.48. Malt 3		
Viscometer 4		
1	15	116.3
2	45	107.3
3	75	99.4
4	105	93.4
5	135	88.2
6	165	83.2



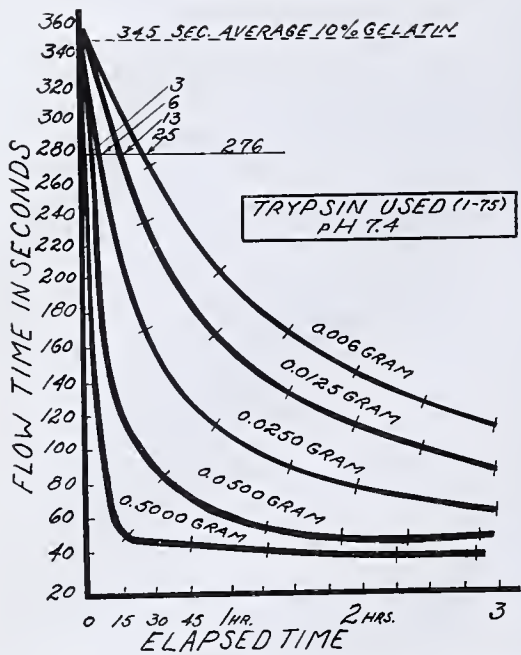


FIGURE 5. EFFECTS OF VARIOUS AMOUNTS OF TRYPSIN (See tables, right)

and many types of proteolytic digestions), a large number of runs were made with pepsin, trypsin, and papain, chosen to cover a wide pH range. The series of curves for trypsin and papain (Figures 5 and 6) indicate that the viscometer gives very dependable results, since activity as determined corresponds to the amount of enzyme present. As a pure unbuffered gelatin was used, its viscosity was taken as initial viscosity and no extrapolation was required.

It is evident that a very satisfactory set of curves is obtained in each instance. Even though the amounts of enzyme differ but little, curves do not cross as they would if possible variables were not automatically kept constant by employing similar viscometers and method of making runs.

The extreme sensitivity is shown by the fact that the upper curve in Figure 5 contains 0.006 gram of trypsin per liter, representing an enzyme concentration of 6 parts per million of substrate.

CHOICE OF A 20 PER CENT VISCOSITY DROP AS THE STANDARD ENZYMATIC CHANGE. In working out a method of this sort it is exceedingly important to note for purposes of comparison the time necessary to produce a given change. As shown in Figures 5 and 6, it would be entirely unsatisfactory to compare the various amounts of activity produced in a given time. As the curves tend to become horizontal, there is very little change in viscosity for a considerable time. This use of comparative times necessary to produce a given change

1,000 Cc. of Substrate. 100 Grams of U. S. Gelatin 7A. pH of Gelatin, 7.4

Run	Elapsed Time Min.	Flow Time Sec.
Viscometer 4, 0.006 Gram of Trypsin		
1	15	320.0
2	45	231.8
3	75	185.6
4	105	163.4
5	135	147.5
6	165	134.3
Viscometer 2, 0.0125 Gram of Trypsin		
1	15	288.3
2	45	196.1
3	75	148.6
4	105	128.2
5	135	118.6
6	165	100.2
Viscometer 3, 0.0250 Gram of Trypsin		
1	15	228.6
2	45	137.8
3	75	105.6
4	105	92.1
5	135	82.6
6	165	78.2
Viscometer 2, 0.05000 Gram of Trypsin		
1	15	118.5
2	45	73.2
3	75	57.9
4	105	56.5
5	135	55.1
6	165	56.6
Viscometer 2, 0.5000 Gram of Trypsin		
1	15	46.8
2	45	44.3
3	75	42.8
4	105	41.8
5	135	42.0
6	165	42.8

coincides with the views of Northrop and Hussey (5), Haldane (2), Tauber (9), Laufer (3), and others (6).

Figures 7 and 8, made from Figures 5 and 6, show very satisfactory agreement between observed and calculated time necessary to produce a 20 per cent drop in viscosity. It was found that a 10 per cent drop was too short a time for reaction, as slight variations in starting runs, transferring solutions, and temperature changes can produce some error. A 30 per cent viscosity drop is also very satisfactory, but there seems to be no justification for the extra time that would be required for runs.

CHOICE OF pH 5 TO 6 AS STANDARD FOR RUNS. In general the plant proteolytic enzymes seem to have a broader optimum activity curve than the animal proteolytic enzymes. Plant proteinases seem to center about an average pH of between 5 and 6 (3, 13).

These enzymes are all similar to papain and are often referred to as papainases. They have an optimum pH of from 4 to 7 (9). Laufer's work was done at a pH of 5 (3).

The authors' experience proved that the variation in activity for pH between 5 and 6 was within the magnitude of experimental error.

The pH at the beginning and end of a run varied only a few hundredths pH, showing that the gelatin was more than amply buffered for the determinations. These considerations simplify procedure to a great extent, as a gelatin with a pH of from 5 to 6 will surely give maximum activity, and buffering is entirely

1,000 Cc. of Substrate, 100 Grams of U. S. Gelatin 7A. pH of Gelatin 7.4

Run	Elapsed Time Min.	Flow Time Sec.
Viscometer 2, 0.050 Gram of Papain		
1	15	377.8
2	45	361.2
3	75	342.1
4	105	322.8
5	135	303.6
6	165	297.6
Viscometer 3, 0.10 Gram of Papain		
1	15	361.0
2	45	323.6
3	75	298.4
4	105	284.4
5	135	277.1
6	165	263.2
Viscometer 3, 0.40 Gram of Papain		
1	15	321.2
2	45	258.4
3	75	226.1
4	105	217.8
5	135	201.4
6	165	190.8
Viscometer 2, 0.50 Gram of Papain		
1	15	287.6
2	45	218.3
3	75	178.2
4	105	158.3
5	135	144.2
6	165	140.1
Viscometer 3, 1.00 Gram of Papain		
1	15	243.8
2	45	137.6
3	75	107.4
4	105	98.7
5	135	92.3
6	165	88.6
Viscometer 4, 1.50 Grams of Papain		
1	15	197.2
2	45	97.8
3	75	79.6
4	105	77.1
5	135	72.6
6	165	61.2

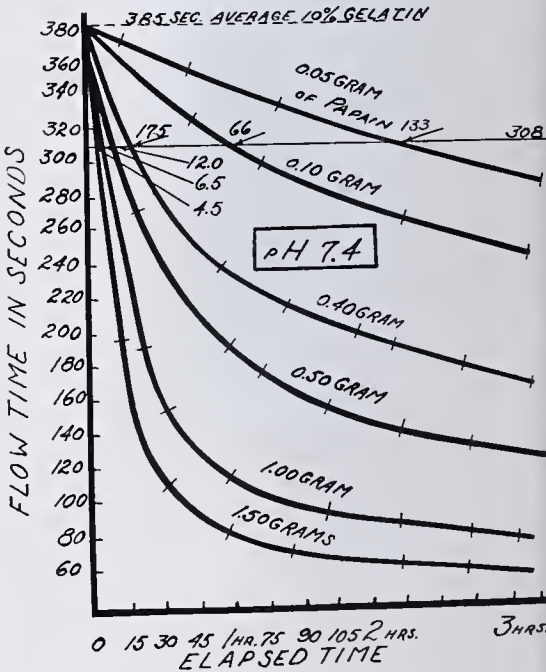


FIGURE 6. EFFECTS OF VARIOUS AMOUNTS OF PAPAIN (See tables, left)



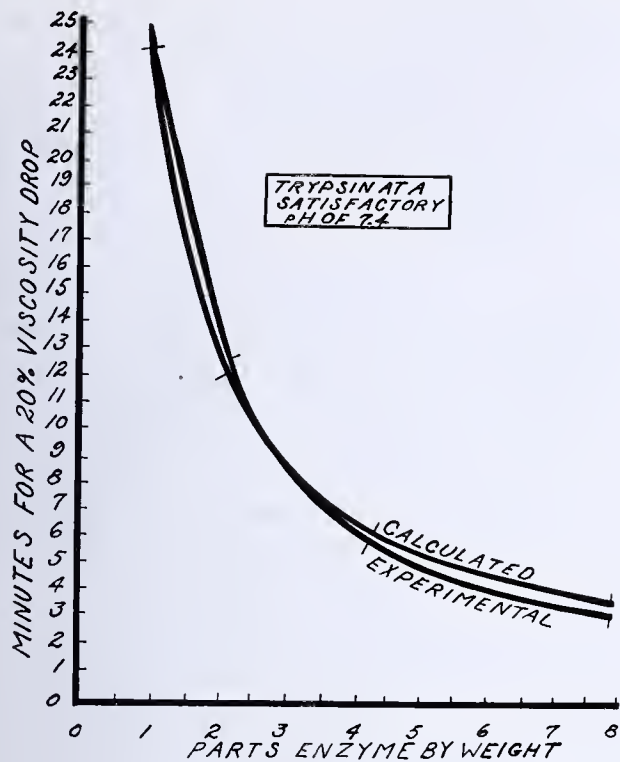


FIGURE 7. TIME REQUIRED FOR 20 PER CENT VISCOSITY DROP, USING TRYPSIN

20% Viscosity Drop		
Parts by Weight of Enzyme	Calculated Min.	Observed Min.
1	25.0	25.0
2	12.5	13.0
4	6.25	6.0
8	3.12	3.0

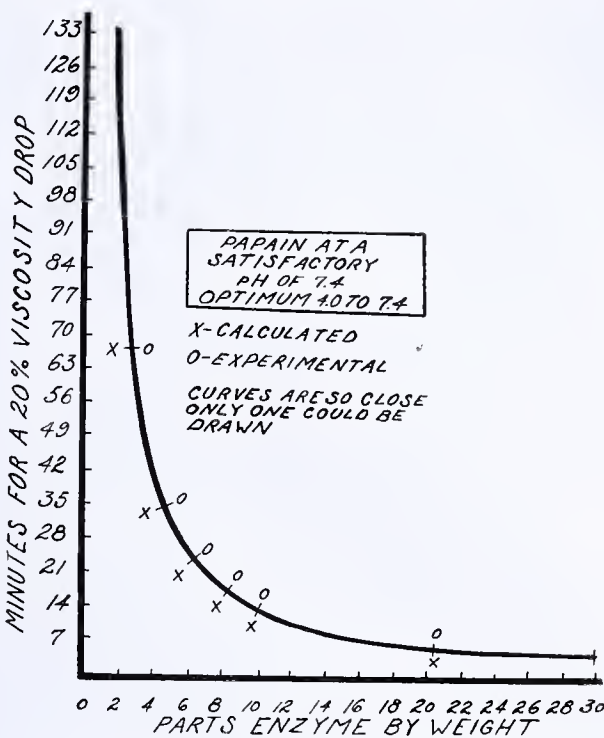


FIGURE 8. TIME REQUIRED FOR 20 PER CENT VISCOSITY DROP, USING PAPAIN

20% Viscosity Drop		
Parts by Weight of Enzyme	Calculated Min.	Observed Min.
1	133.00	133.0
2	66.50	66.0
4	33.25	33.0
6	22.60	22.0
8	16.60	17.5
10	13.30	12.0
20	6.60	6.5

unnecessary. With the addition of no foreign agents what-  
ever, retardation or activation of the enzymes in malt is out  
of the question.

Standardization of Viscometers in Kinematic Viscosity

In order to clarify the presentation, the standardization of  
viscometers has been postponed to this point. The fact that  
only one temperature is used simplifies the necessary calcula-  
tions to a considerable extent. Only two liquids need be  
used and the following sample calculations give the necessary  
constants.

Undoubtedly one will use only kinematic viscosities as  
soon as he has become accustomed to making the determina-  
tions. The value for proteolytic activity,  $P_m$ , is calculated  
in terms of the time necessary for a 20 per cent drop in kine-

matic viscosity and comparisons can then be made with  
any laboratory. Graphs similar to Figure 9 allow the ready  
conversion of flow time to kinematic viscosity. Such con-  
versions were made in calculating the proteolytic activities

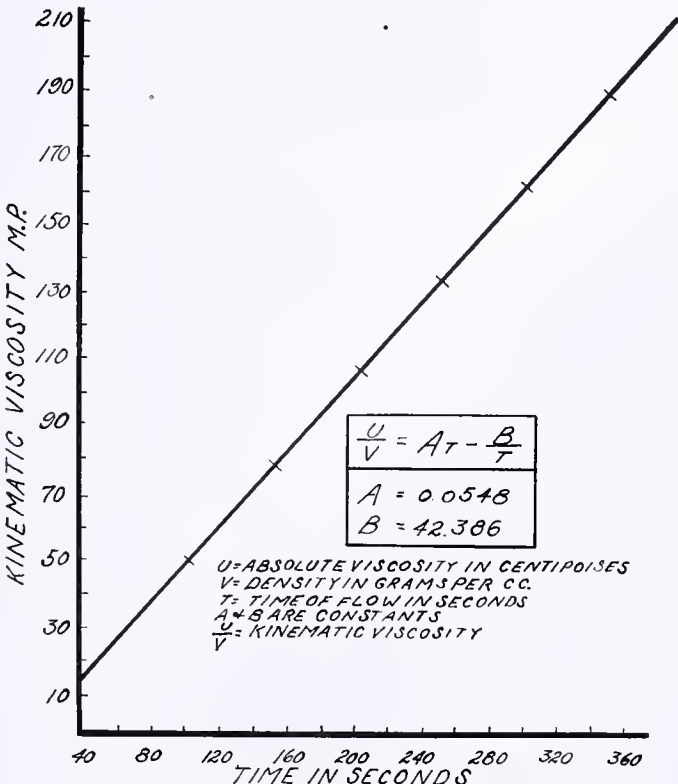


FIGURE 9. VISCOMETER CALIBRATION CURVE  
(See table, left)

Conversion of Time to Kinematic Viscosity, Viscometer 1

Time Sec.	Kinematic Viscosity Millipoises	Time Sec.	Kinematic Viscosity Millipoises
40	11.32	200	107.48
50	18.92	210	113.10
60	25.81	220	119.22
70	32.30	230	124.83
80	38.76	240	130.00
90	44.61	250	135.30
100	50.56	260	140.90
110	56.42	270	145.23
120	62.23	280	152.00
130	67.82	290	157.50
140	77.97	300	162.98
150	79.37	310	168.82
160	85.00	320	174.00
170	90.64	330	179.80
180	97.06	340	185.00
190	102.80	350	190.59



of the pure variety malts and the commercial malts as given in the tables.

Water and a 40 per cent sucrose solution have been found convenient liquids for standardization. The runs as described above give the number of seconds for 50 cc. to flow. This number of seconds is converted into kinematic viscosity by means of two constants, *A* and *B*, which are determined for the viscometer in question.

TABLE I. TYPICAL VALUES	
20% Kinematic Viscosity Drop	<i>P<sub>m</sub></i>
Min.	
50	200
80	170
110	140
140	110
170	80
200	50
230	20
250	0

Kinematic viscosity =  $At - \frac{B}{t}$ , where *t* is time in seconds and *A* and *B* are constants.

The kinematic viscosities at 40° C. are found in tables prepared by Sheely (8).

Water at 40° C., 0.662  
40% sucrose at 40° C., 2.94

It only remains to solve for *A* and *B* as follows:  
Time for water at 40° C., 34.5 seconds  
Time for 40 per cent sucrose at 40° C., 65.4 seconds  
Then, for sucrose

$$2.94 = A65.4 - \frac{B}{65.4}$$

Clearing,

$$192.423 = A4283.7 - B \tag{1}$$

For water,

$$0.662 = A34.5 - \frac{B}{34.5}$$

Clearing,

$$22.839 = A1190.25 - B \tag{2}$$

Subtracting 2 from 1,

$$169.584 = 3093.45A$$
$$A = 0.0548$$

Now solve for *B* by substituting the value of *A* in Equation 1 or 2. Taking 2

$$22.839 = 1190.25 \times 0.0548 - B$$
$$B = 42.386$$

Having *A* and *B*, the equation is solved for different flow times and a graph similar to Figure 9 is made. Once having the calibration curve, no further calculations are necessary and the kinematic viscosity for any flow time is easily read from the chart. For comparison, a 20 per cent drop in kinematic viscosity is now taken instead of a 20 per cent drop in seconds of flow.

CALCULATION OF UNIVERSAL VALUES FOR PROTEOLYTIC ACTIVITY OF MALTS, *P<sub>m</sub>*. The values of *P<sub>m</sub>* here given are calculated in accordance with suggestions made by chemists in the Froedtert and other malting laboratories. They are very comparable to "diastatic power" figures as used today and should be given ready acceptance. They are based on kinematic viscosity figures and are therefore readily duplicated in any laboratory. The same malt will have the same *P<sub>m</sub>* value, no matter where tested.

Diastatic power, proof of spirit, and other similar figures familiar to the brewing industry run to about 200 as a maximum value, the increase in numerical value meaning an increase in the property in question.

The proteolytic strength of malt varies inversely with the time required to effect a 20 per cent drop in kinematic viscosity. Thus a malt that produces a 20 per cent drop in viscosity in 50 minutes has a higher proteolytic value than a malt that produces a 20 per cent drop in 100 minutes. A proteolytic activity of 200 is given to a malt that produces a 20 per cent drop in 50 minutes. A proteolytic activity of 0 is given to a malt that produces a 20 per cent drop in 250 or more minutes. Thus we have a range of 200 minutes (250 - 50) in 20 per cent kinematic viscosity drop against a range of 200 points in terms of proteolytic activity. Thus a one-minute increase in the time required to effect a 20 per cent drop in viscosity is equivalent to a decrease of one point in proteolytic activity.

TABLE II. PURE VARIETY MALTS																
Variety	Oder.	Oder.	Oder.	Ped.	Ped.	Ped.	Ped.	Velvet	Velvet	Velvet	Velvet	Manch.	Manch.	Manch.	Manch.	Peat-
Locality	Wis.	Waseca, Minn.	Ill.	#38 Wis.	#38 Waseca, Minn.	#38 Ill.	#38 Mont.	Madi-son, Wis.	Minn.	Ill.	Mont.	Wis.	Minn.	Ill.	Mont.	land Wis.
Barley No.	Control	...	...	Control	...	...	...	...	...	...	...	...	...	...	...	...
Malt No.	934	958	881	920	876	887	857	933	930	879	872	939	957	890	830	932
1,000 kernel weight of malt (dry basis)	23.2	20.8	25.73	22.8	20.5	22.87	31.92	20.39	22.1	24.98	28.98	21.34	19.62	23.25	25.75	19.41
Growth of malt:																
Dead	...	4	1	...	7	5	3	1	0	1	0	2	4	1	0	0
0-1/4	...	1	1	...	0	2	11	1	1	1	2	6	0	0	0	0
1/4-1/2	...	2	8	...	8	9	19	4	18	20	26	11	2	3	8	34
1/2-3/4	...	63	62	...	58	61	46	35	50	62	49	45	26	72	58	45
3/4-1	...	30	28	...	26	23	21	59	30	15	23	35	66	24	33	21
Over 1	...	0	0	...	1	0	0	0	1	0	1	2	0	1	0	0
Exposed acrospires	...	10	11	...	22	4	3	5	8	11	14	1	17	6	12	6
Moisture of dried malt	4.5	4.5	4.0	4.4	4.0	4.4	5.2	4.6	4.4	4.4	5.0	4.4	5.0	4.9	6.2	4.5
Character of endosperm:																
Steely	...	0	0	...	0	0	0	0	0	0	0	0	0	0	0	0
Half steely	...	8	4	...	0	0	22	1	20	4	39	3	13	0	3	2
Mealy	...	92	96	...	100	100	78	99	80	96	61	97	87	100	97	98
Index of mellowness	98.0	96.0	98.0	100.0	100.0	100.0	89.0	99.5	90.0	98.0	80.5	98.5	93.5	100.0	98.5	99.0
Extract of malt (dry basis)	73.2	71.7	75.7	67.9	70.3	73.4	72.9	72.0	70.7	75.8	71.6	72.2	72.3	76.4	74.9	72.0
Time of inversion	7	>5	7	10	5	10	7-10	7	>5	5	5	>5	>5	5	>5	7-10
Filtration time	13	14	24	9	15	14	11	17	15	19	13	13	16	17	10	15
Color of wort	1.4	1.5	1.3	1.4	1.4	1.4	1.1	1.5	1.5	1.4	1.2	1.4	1.5	1.4	1.3	1.5
Total N of malt	1.97	2.49	1.68	2.12	2.36	1.54	2.30	2.02	2.56	1.76	2.30	2.10	2.56	1.73	2.25	2.16
Total protein of malt	12.34	15.53	10.52	13.22	14.70	9.64	14.34	12.63	15.96	11.01	14.37	13.13	16.00	10.83	14.02	13.50
Soluble N of wort	0.662	0.890	0.630	0.591	0.610	0.510	0.520	0.730	0.850	0.680	0.560	0.750	0.910	0.640	0.800	0.690
Soluble N as protein of wort	4.13	5.58	3.94	3.69	3.83	3.19	3.25	4.55	5.31	4.23	3.49	4.68	5.68	3.98	5.03	4.33
Formol nitrogen	0.130	0.178	0.111	0.094	0.098	0.089	0.081	0.154	0.175	0.135	0.089	0.154	0.188	0.118	0.155	...
Soluble N, % of total N	33.60	35.86	37.56	27.88	25.97	33.25	22.65	36.04	33.24	38.58	24.30	35.71	35.35	36.94	35.73	32.08
Formol nitrogen, % of wort N	19.64	19.93	17.59	15.91	15.99	17.38	15.55	21.15	20.56	19.88	15.92	20.53	20.77	18.47	19.28	...
Diastatic power	127	212	113	97	110	74	155	123	171	95	162	153	207	118	259	118
Proteolytic activity, <i>P<sub>m</sub></i>	149	157	141	88	99.5	111	53.5	169.5	167	134	60.5	153.5	172.5	154	141	179.5



Formula for calculating proteolytic activity,  $P_m$ :

$$P_m = 250 - t$$

where  $P_m$  represents the proteolytic activity of the malt and  $t$  the time in minutes for a 20 per cent drop in kinematic viscosity.

As is evident from the above expression, each minute required for the 20 per cent drop in kinematic viscosity decreases the value of  $P_m$  by one point (Table I).

Proteolytic Activity of Malts of Known Composition

Table II indicates constants ordinarily determined, together with the new proteolytic activity of malt figures,  $P_m$ . Even though these results have been carefully checked, they are significant only for these particular samples. Since they are pure varieties, they may differ widely from commercial samples and also from a pure variety grown under different climatic conditions.

Table II shows that one may expect more variation in proteolytic value of pure variety than in the ordinary run of commercial malts. Undoubtedly the smaller quantity of barley and small-scale processing would allow for more variation. The common practice of blending commercial malts would tend to make for some uniformity. Some of the extremely low proteolytic values in the pure varieties may have been caused by a dry season or a poor soil. Commercial malts naturally come from favorable localities.

Inspection of Table II will show proteolytic values between 53.5 and 179.5 for the pure varieties, while in Table III the values run between 172 and 204.

Acknowledgment

The pure variety malts and the major portion of data in Table II were furnished through the courtesy of J. G. Dickson of the University of Wisconsin Agricultural Experiment

TABLE III. PROTEOLYTIC ACTIVITY OF REPRESENTATIVE COMMERCIAL MALTS

Malt	Time Required for 20% Kinematic Viscosity Drop Min.	Proteolytic Activity $P_m = 250 - t$
1	46	204
2	78	172
3	76	174
4	52	198
5	72	178
6	77	173
7	76	174
8	52	198
9	50	200
10	46	204

Station. The work is supported in part by a grant from the United States Maltsters Association.

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RECEIVED March 26, 1938. A contribution from the chemical laboratories of Marquette University and Froedtert Grain and Malting Company, Inc.

A Laboratory Mashing Apparatus

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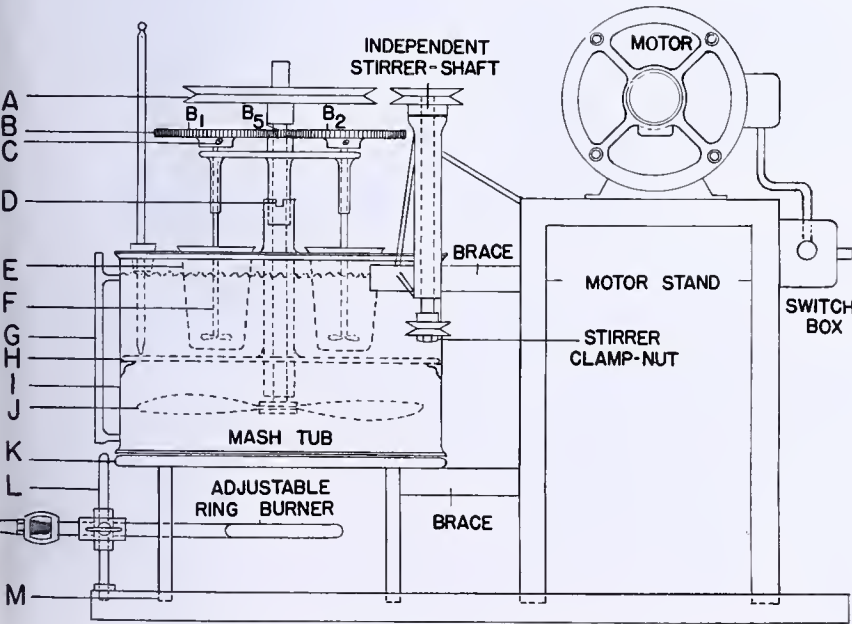


FIGURE 1. SIDE VIEW OF APPARATUS

MALT and cereal analysis for total extract, the sugar-dextrin ratio, conversion time, and the color of the wort are a routine operation for brewery laboratories. The test, as described by the Malt Analysis Standardization Committee of the American Society of Brewing Chemists, specifies strict limitations of time and temperatures, as well as continuous stirring, held within narrow limits as to speed. Since the total time required for a malt analysis is 1 hour and 55 minutes, with an additional 10 minutes for cooling, it is obvious that some kind of mechanical assistance, with at least partial automatic temperature control, is needed.

There are a number of machines on the market for this purpose, but their high price militates against their general use, especially in the smaller commercial laboratories and those breweries where only one or two samples per week are required to be analyzed. A labora-



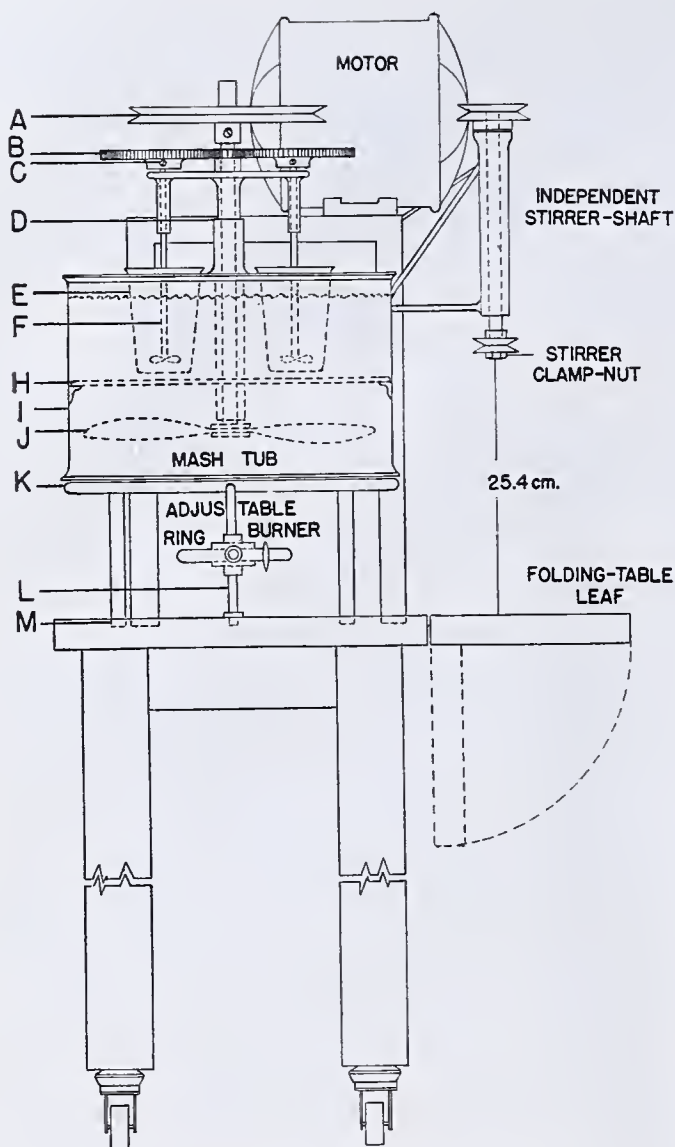


FIGURE 2. END VIEW OF APPARATUS

tory is usually unwilling to invest two to three hundred dollars in a piece of equipment that has such little and specialized use.

To meet the need for a low-cost mechanical mashing apparatus with semiautomatic temperature controls, the device described below was constructed. It is adaptable to a number of other uses besides that of mashing, and as such becomes a valuable piece of general laboratory equipment—for example, the introduction of an independent stirrer shaft serves, on the one hand, for occasional use as a stirrer and on the other as a motive source from which a ball mill or a shaking machine may be run. The pulleys are all interchangeable and may be run directly off the

motor or through the mash-tub shaft, thus enabling the attainment of any desired speed. The four main brass mashing stirrers are easily removable and may be replaced by glass ones for use in other kinds of chemical reactions.

The cost of the entire machine, including labor of construction and the motor, did not exceed \$50.00.

Figures 1, 2, and 3 show the side, end, and top views, respectively, of the apparatus.

In Figure 1, the large pulley, A, is run by belt from the motor and activates the gear system, B, through gear B<sub>1</sub>. It is connected to the water paddle, J, through the loose slotted joint at D. The entire gear system and pulley may thus be lifted out to give access to the beakers, E. The brass stirrers, F, may be replaced by glass or other types by loosening the setscrew, C, beneath the gears, B<sub>1</sub>, B<sub>2</sub>, etc. G is a water-level tube. The perforated false bottom, H, and the stirrer, J, form a unit with the central shaft bearing and top of the mash tub. The top overlapping the tub slightly, and the false bottom, resting upon four brackets, I, give to this system the desired rigidity. The mash tub rests upon the frame, K, and is additionally supported and held in place by two braces. Two thermometer wells (Figure 3) are placed diametrically opposite each other in the top, and also serve during cooling, water being introduced through one and siphoned out through the other. Thermometers, which dip into the mash beakers for determination of mash temperatures, are held by buret clamps attached to the four stirrer-shaft housings. Tests have been run on the time required to cool the water bath. Running water at 15° C. into one thermometer well and siphoning out through the other, starting at 70° C. and using tubing 0.8 cm. in inside diameter, it required 4 minutes to bring the temperature down to that of the cooling fluid. The use of a larger or smaller siphon tube would decrease or increase this time.

The whole frame, including the motor stand, may be removed from the table by lifting the eight legs out of their drilled holes, M.

The 10-cm. (4-inch) ring burner is adjustable on its supporting stand, L, and is an adequate source of heat for all details of the analysis. Temperatures with variations not exceeding  $\pm 0.25^\circ$  C. may be maintained for any desired length of time by carefully controlling the height of the burner and the flame.

Gears and pulleys of convenient size are obtained by use of a low-speed motor. In the present apparatus with a motor of 1165 r. p. m. and a pulley of 3.17 cm. (1.25 inches), an 18.41-cm. (7.25-inch) pulley, A, on the mash tub is needed. The gear ratio, B<sub>1</sub> to B<sub>2</sub> (diameters), is 5.71 cm. (2.25 inches) to 12.06 cm. (4.75 inches). This gives to the stirrers the satisfactory speed of 95 r. p. m., which, coupled with a rather high pitch of the blades, is sufficient to swirl the water gently throughout.

The mash tub is made of 22-gage copper and its size is governed by the number of beakers it is to accommodate. For four standard malt beakers a diameter of 32 cm. (12.5 inches) and a height of 19.7 cm. (7.75 inches) are satisfactory. The false bottom rests 10.2 cm. (4 inches) below the top, and the length of the mashing paddles is 20.3 cm. (8 inches).

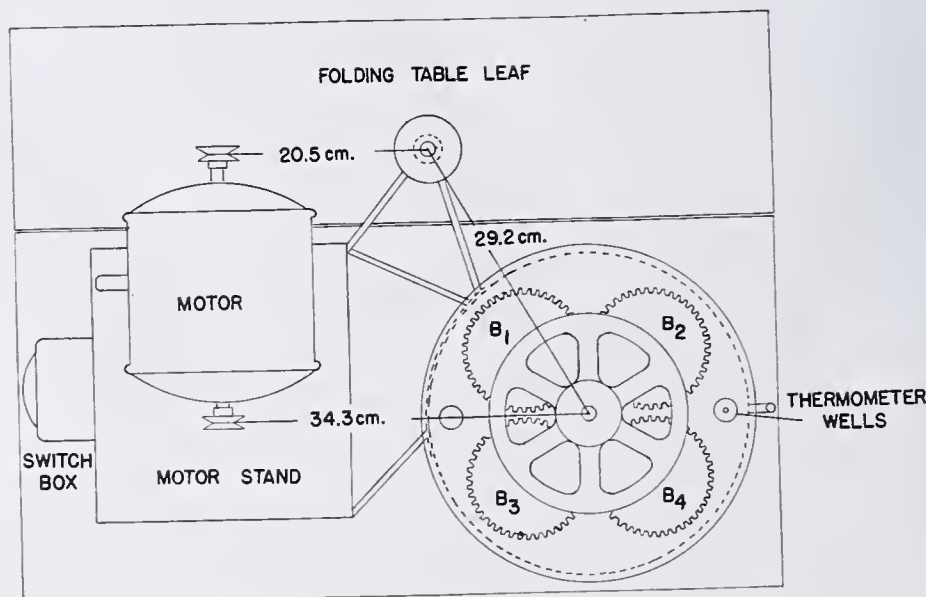


FIGURE 3. TOP VIEW OF APPARATUS

## Acknowledgment

Acknowledgment is gratefully made to Edward Ehmke for the drawings of the apparatus.

RECEIVED August 30 1938.



# A Compact Field Laboratory for Sanitary Chemistry

JAMES G. WEART, Illinois Department of Public Health, Springfield, Ill.

THIS field laboratory was designed for the use of sanitary engineers engaged in the wide variety of problems encountered by the Department of Public Health and the State Sanitary Water Board. These problems include the supervision of all types of water-treatment plants and sewage plants, and the investigation of industrial wastes and stream pollution.

For these purposes, the kit was designed to permit the following tests: pH, dissolved oxygen, alkalinity, soap hardness, residual chlorine, carbon dioxide, and temperature. Sufficient extra capacity is provided so that it can be readily adapted to test for iron, nitrites, copper, or ammonia.

## Apparatus and Methods

The case is substantial. Top, sides, and bottom are constructed of 1.25-cm. (0.5-inch) birch. The finish inside and out is acid- and alkali-resistant. A full-length piano hinge and trunk clasps support the cover. All corners are closed with a lock or pin box joint. Top and bottom corners are protected with trunk corners.

In the field, a clean work table is provided by the lid of the case, which is supported by two metal rods which screw into metal floor sockets. The inside of the lid is covered with white celluloid.

The buret support rod is screwed into another floor socket. The buret clamp is readily attached.

For burets, 10-ml. serological pipets are adapted by a modification of an old device, a bead in a rubber tube. The bead is located at the upper end of the pipet instead of at the bottom. This permits easy filling and excellent control during titrations. There are no stopcocks to break. Three of these pipet-burets, one for each of the three standard solutions, are held by clips in the removable tray.

The test most frequently made in this work is the determination of pH. The kit provides for the colorimetric determination of pH over the range of 4.0 to 11.0, in steps of 0.2 pH. For demonstration tests and approximations, a wide-range indicator is provided. In the range from pH 6.4 to 8.4, which is used most frequently, the two indicators required are supplied in 59-ml. (2-ounce) bottles. All other indicators are in 9.6-ml. (1-ounce) bottles. As but one or two drops of indicator are needed for each

test, the amount of indicator supplied is ample. This type of pH equipment was designed about ten years ago at the laboratories of the Sanitary District of Chicago.

The regular Winkler method is used for dissolved oxygen. The reagents are in Pyrex dilution bottles of 180-ml. capacity, and are dispensed by a Pyrex pipet graduated at 0.5 and 1.0 ml., fitted in a rubber stopper, and operated by a rubber bulb. Two 118-ml. (4-ounce) ground-glass stoppered bottles, graduated at 100 ml., are provided for the collection of samples and for the test. Sulfuric acid is supplied in 50 per cent strength, rather than concentrated, so that 1 ml. can be added to fill the neck of the bottle. Fifty to sixty dissolved oxygen determinations can be made with the solutions provided.

Alkalinity and soap hardness are determined according to standard methods (2). For the measurement of samples there are a graduate and a calibrated bottle. Distilled water is available for dilution purposes.

Free carbon dioxide can be calculated from the alkalinity and pH, according to the formula of DeMartini (1):

$$\log \text{CO}_2 = 6.2874 + \log (\text{HCO}_3^- \text{ as CaCO}_3) - \text{pH}$$

A slide rule or a log table is, of course, necessary.

For residual chlorine, standards prepared from Scott's buffered chromate-dichromate solutions are provided.

The *o*-tolidine furnished contains 20 per cent hydrochloric acid. Tests are made in 59-ml. (2-ounce) oil sample bottles.

For adaptations to special work, two dropping bottles, three 59-ml. (2-ounce) oil sample bottles, and one dilution bottle are provided as surplus. Two spare dosing pipets with bulb and rubber stopper are included.

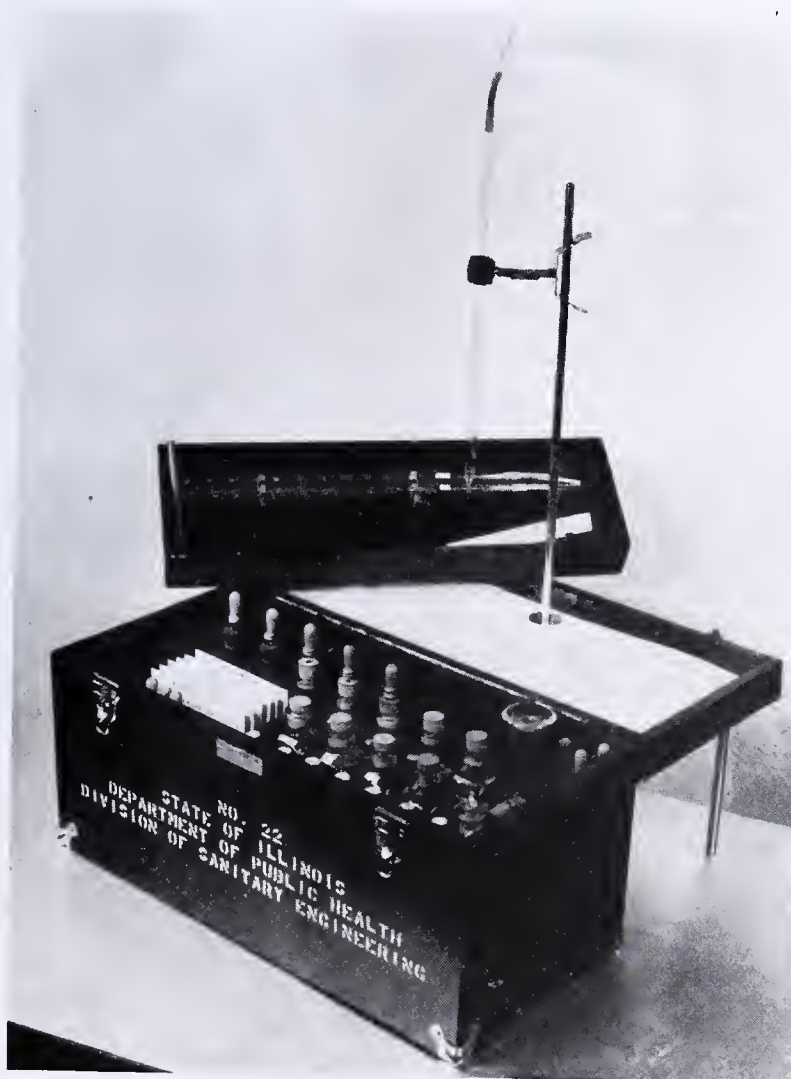
The kits were prepared by Rascher & Betzold at a cost of \$90 each in lots of ten. The weight is 13.6 kg. (30 pounds).

No claim for perfection is made, and suggestions for improvement are invited.

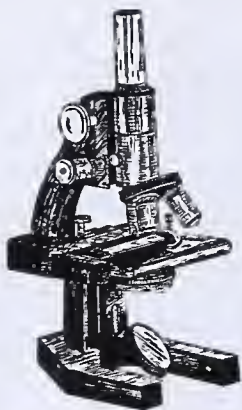
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# Microchemistry

## Determination of Density Differences

### By the Flotation Temperature Method

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A description of the construction and manipulative details of a flotation temperature apparatus as used for analytical purposes is given. Of particular interest is the development of the flotation temperature determination as a density micro-method. The flotation temperature can be determined to within  $0.005^{\circ}\text{C}$ . in samples as small as 0.1 ml.

A method of calculating densities and compositions from flotation temperatures is discussed, which includes a consideration of the thermal expansion of the float, changes of the temperature of flotation in the reference sample, and deviations from ideal solution laws. The design of a special slide rule for calculating the percentage composition from the flotation temperature is indicated.

THE flotation temperature method for determining small differences in density was developed by Richards and co-workers (8, 9) into a precision method. It is used regularly in the isotopic analysis of heavy water (3, 5). In connection with a survey of the isotopic ratio of deuterium to hydrogen in water from various sources, Briscoe and co-workers (1) have described details and improvements of the method which make it more rapid and workable.

In the course of separation of isotopic forms of water the authors have found it necessary to devise "flotation temperature" apparatus which will handle very small samples of water. At the same time they have found certain methods of calculation to be time-saving in the treatment of results. This paper presents their conclusions as to these details of the flotation temperature method.

#### Apparatus

Figure 1 gives a diagrammatic view of the present apparatus as developed in this laboratory. The manual control of temperature is not proposed as any improvement over the automatic control described by Briscoe and others (1); the apparatus is easier to build, but the temperature control is

somewhat less certain. The temperature readings are also made less certain, because the temperature of the sample itself cannot be determined directly, if it is desired to use small volumes of a sample. Nevertheless the flotation temperature as read from the Beckman thermometer is reproducible to within  $0.005^{\circ}\text{C}$ ., which is sufficiently accurate for most purposes.

The electric buzzer, *L*, is used to agitate both the thermometer and the sample tube. This prevents sticking of the float and the mercury column of the Beckman thermometer. The copper wire, *O*, was originally used to dislodge the float when it became stuck, but with the buzzer it is not needed.

The sample, previously purified by distillation first over alkaline permanganate, then from phosphoric acid, and finally by outgassing, is placed in the tube, *A*, which contains the Pyrex float, *B*. Then the temperature of the bath is alternately raised and lowered until the temperature limits, above which the float sinks

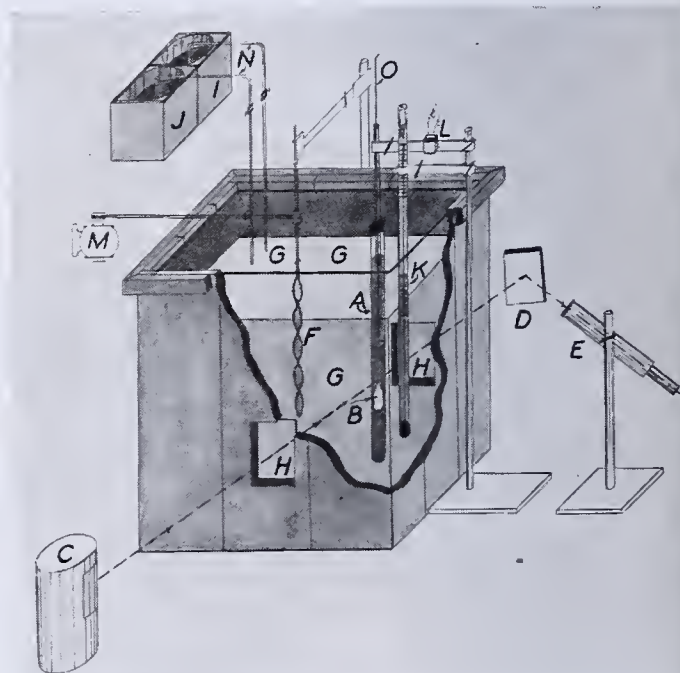


FIGURE 1. FLOTATION TEMPERATURE APPARATUS

- |                              |                             |
|------------------------------|-----------------------------|
| A. Sample test tube          | I. Thermostat control, cold |
| B. Density float             | J. Thermostat control, hot  |
| C. Light                     | K. Beckman thermometer      |
| D. Mirror                    | L. Buzzer                   |
| E. Telescope with cross hair | M. Motor                    |
| F. Stirrer                   | N. Siphons                  |
| G. Thermostat                | O. Float regulator          |
| H. Window                    |                             |



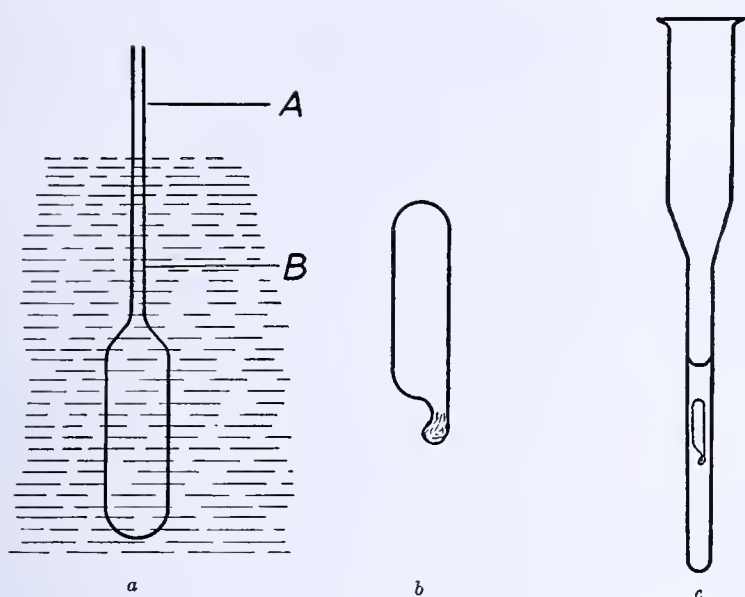


FIGURE 2. MICROFLOAT AND MICROFLOTATION TUBE

Sample tubes have also been constructed which are directly connected to the microdistillation apparatus to avoid losses of material.

With microfloats and sample tubes constructed in this way, the authors have been able to determine the flotation temperature of samples as small as 0.1 ml. as accurately as with large samples in the usual way. This has been verified by control analyses in which the same sample was tested with different floats and sample tubes.

### Calculation of Densities and Compositions

Both the density of the sample and the density of the float change with temperature. The flotation temperature is the temperature at which the two densities are the same.

In Figure 3, curve *B* represents the density of the sample as a function of temperature, while curve *F* represents that of the float. The inter-

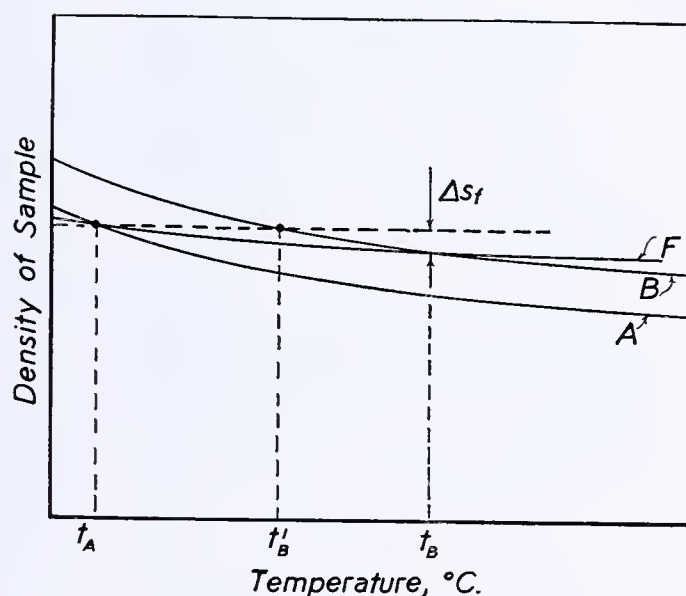


FIGURE 3. RELATION OF DENSITY TO FLOTATION TEMPERATURE

and below which it rises, are brought to within 0.005° C. In routine analysis for control purposes only, the distillation from phosphoric acid is dispensed with unless the ammonia content of the sample is known to be high.

In agreement with Briscoe and others (1) the authors have found that removal of dissolved carbon dioxide from the sample by heating it to 50° C. under vacuum with agitation materially alters the observed flotation temperature.

### Microfloats

The microfloats are constructed from thin-walled tubing obtained by drawing out the central portion of a Pyrex test tube to about 2-mm. outside diameter. This tube is sealed at one end and then the other end is drawn out to a fine long capillary about 3 to 4 mm. away from the sealed end.

The most difficult problem is to adjust the density of the float so that it will just float in a standard reference sample—e. g., normal water—at a reasonable temperature. The uncompleted float is placed in a small quantity of the standard sample at the desired temperature. As shown in Figure 2a, it rides a little low. If the capillary is broken off at *A*, the float will rise until point *B* is at the level of the surface.

If the portion which projects above the surface is now melted down into a small drop very close to *B*, the float will still ride with *B* just at the surface. Further melting down of the capillary diminishes the volume of the float sufficiently that eventually it will just barely sink. With a little practice this can be done in such a way that the desired adjustment of flotation temperature in the standard sample is obtained in a short time. If the capillary is melted down too much, the bulb may be heated just to the softening point; the internal pressure will then cause the bulb to expand very slightly. Very fine adjustment may be obtained by scratching the glass drop very lightly with a file.

It is impossible to obtain sufficiently fine adjustment by using a mercury ballast, since sealing the float causes sufficient change in volume to destroy the adjustment entirely. For this reason the use of mercury ballast is of no value. The method described is the only one which has been found to give satisfactory adjustment without too much effort.

The completed float should preferably have the shape shown in Figure 2b. With this shape it will float stably in an upright position, owing to the extra weight of glass in the drop at the bottom. Otherwise it will tend to float diagonally and wedge in the sample tube. Floats have been made in this way which are about the size of a grain of wheat.

The sample tube is made as shown in Figure 2c. Its internal diameter is the smallest in which the float will move freely. By using the buzzer, *L*, the authors have been able to use extremely small clearances without materially affecting the accuracy of the determination. The only disadvantage of a small clearance which they have observed is that the float reacts more slowly to density changes, so that the total time of a determination is increased from the usual 10 minutes to about 15 minutes for the microfloats.

section of the two curves corresponds to the temperature  $t_B$ . This is the temperature at which float and sample have the same densities, and hence is the flotation temperature. Curve *A* represents the density of another sample whose flotation temperature is  $t_A$ .

If the density of the float were constant, as represented by the horizontal dotted line, the flotation temperature of sample *B* would be  $t_B'$  instead of  $t_B$ . The flotation temperatures of a group of samples would then be the temperatures at which the samples all have the same density, equal to that of the float.

Actually, the density of sample *B* at its flotation temperature is less than that of sample *A* at its flotation temperature by the amount  $\Delta s_f$ . The ratio  $\Delta s_f/(t_A - t_B)$  is the average thermal coefficient of the density of the float over the temperature interval  $(t_A, t_B)$ . If the bob expands linearly with temperature according to the equation

$$V_f(t_B) = V_f(t_A)[1 + a(t_B - t_A)] \quad (1)$$

where  $a$  is the coefficient of cubical expansion of the float, then the ratio,  $s_f(t_B)/s_f(t_A)$ , of densities of the float at the two temperatures is

$$s_f(t_B)/s_f(t_A) = V_f(t_A)/V_f(t_B) = \frac{1}{1 + a(t_B - t_A)} \quad (2)$$



Since the coefficient of expansion,  $\alpha$ , of glass is very small, this expression may be rewritten to a high degree of approximation as

$$\Delta s_f = s_f(t_A) - s_f(t_B) \cong s_f(t_A) \alpha (t_B - t_A) \quad (3)$$

Richards (8, 9) has proposed the use of the flotation temperature method as a means of determining the coefficient of expansion of the float. The method would consist in preparing a float of the desired material and determining its flotation temperatures in two standard liquids whose densities are well known over a wide temperature range. Equation 3 may then be used to calculate  $\alpha$ , the desired coefficient.

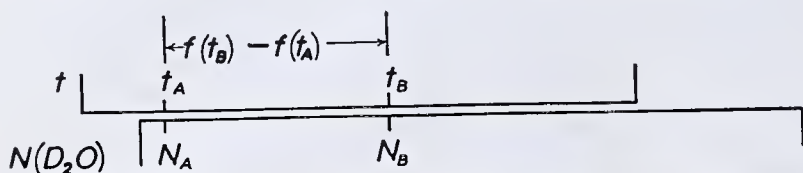


FIGURE 4. SLIDE RULE FOR CALCULATION OF MOLE FRACTION OF DEUTERIUM OXIDE FROM FLOTATION TEMPERATURE

Referring again to Figure 3, the difference in density between substance A and substance B at the temperature  $t_B$  is given as

$$s_B(t_B) - s_A(t_B) = \{s_A(t_A) - s_A(t_B)\} - \Delta s_f \quad (4)$$

If the density,  $s_A(t_A)$ , of substance A is known accurately over the working range of temperature, Equation 4 may be used in calculating the density of the substance B at the temperature  $t_B$ .

Longworth (6) has recently redetermined the densities of mixtures of  $\text{H}_2\text{O}^{16}$  and  $\text{D}_2\text{O}^{16}$  at  $25^\circ\text{C}$ . He concludes that the mole fraction of  $\text{D}_2\text{O}^{16}$  in a sample may be obtained from the value,  $\Delta s$ , of the increase in density of the sample over that of normal water by the equation

$$N(\text{D}_2\text{O}) = 9.2351 \Delta s / (1 - 0.0309 \Delta s) \quad (5)$$

From the data of Lewis and Macdonald (4) as recalculated by Farkas (2) it is seen that, for pure  $\text{D}_2\text{O}$ ,  $\Delta s$  varies by less than four parts per thousand over the range from  $15^\circ$  to  $35^\circ\text{C}$ ., in which flotation temperatures of water are usually determined. In the more dilute solutions the percentage variation of  $\Delta s$  with temperature in this range should be about the same or less. Hence to within 0.5 per cent Equation 5 also holds for temperatures other than  $25^\circ\text{C}$ . in this interval.

For dilute solutions in which the density increment,  $\Delta s$ , is less than 0.05—i. e., solutions containing less than 0.50 mole fraction of  $\text{D}_2\text{O}$ —Equation 5 may be written to sufficient approximation as

$$N(\text{D}_2\text{O}) = 9.235 \Delta s \quad (6)$$

Furthermore, if substance A is taken as normal water, Equation 4 gives  $\Delta s$  for sample B at the temperature  $t_B$  which is ordinarily in the range from  $15^\circ$  to  $35^\circ\text{C}$ . The two equations may therefore be used to calculate the mole fraction  $N(\text{D}_2\text{O})$  of  $\text{D}_2\text{O}$  in the sample from the observed flotation temperatures if the difference is known to be due only to  $\text{D}_2\text{O}$ .

These calculations may be simplified by the use of a specially constructed slide rule. For Pyrex glass floats  $\alpha$  is  $9.6 \times 10^{-6}$  per  $^\circ\text{C}$ . The density  $s_f(t_A)$  is adjusted equal to that of normal water at some convenient temperature,  $t_A$ , preferably between  $20^\circ$  and  $25^\circ\text{C}$ . The term  $\Delta s_f$  is always relatively small, so that  $s_f(t_A)$  may be taken with sufficient accuracy as unity for any temperature in this range (actually it lies between 0.997 and 0.998). Hence,  $s_f \cong 9.6 \times 10^{-6} (t_B - t_A)$ , and  $\Delta s$  for the sample at  $t_B$  is given as

$$\Delta s = [s_A(t_A) - 9.6 \times 10^{-6} t_A] - [s_A(t_A) - 9.6 \times 10^{-6} t_B]$$

The slide rule is constructed by laying off a nonuniform temperature scale on one slide and a mole fraction scale on the other, as shown in Figure 4. The temperature scale is obtained by plotting values of the function

$$f(t) = s_A(t) - 9.6 \times 10^{-6} t$$

for even decimal values of the temperature. The densities,  $s_A(t)$ , of normal water may be obtained from the International Critical Tables for the desired temperatures, without interpolation. The mole fraction scale is a uniform scale whose unit is  $1/9.235$  times the unit used in plotting the function,  $f(t)$ . The slide rule is used by placing the temperature  $t_A$  over the mole fraction  $N_A$  of  $\text{D}_2\text{O}$  in the standard sample, and reading the mole fraction,  $N_B$ , of  $\text{D}_2\text{O}$  in the sample opposite the flotation temperature,  $t_B$ , of the sample.

In calculating the mole fraction of  $\text{H}_2\text{O}^{18}$  in a sample from the flotation temperature, when the sample contains only  $\text{H}_2\text{O}^{18}$  in amounts essentially different from normal water, the same method may be used. However, if we assume the density of pure  $\text{H}_2\text{O}^{18}$  to be 1.111 [Randall and Longtin have found some slight evidence in favor of this value, from studies of the refractive index of water enriched in  $\text{H}_2\text{O}^{18}$  (?), the factor 9.235 for proportionality between mole fraction and density must be replaced by 9.00.

If the approximations assumed in analysis of heavy water cannot be applied, the calculations of compositions may still be carried out accurately by means of the graphical construction of Figure 3. For this purpose a series of density curves—e. g., A and B—is drawn, one for each mole fraction of solute. Then for a particular float the appropriate curve  $F$  is drawn. Corresponding to any particular flotation temperature,  $t_B$ , a point on the curve  $F$  is located. The mole fraction of solute in the sample is read from the solution density curve which passes through this point. The same diagram may be used for different floats by drawing in a different curve,  $F$ , for each float. This method does not involve any assumptions as to linear expansion of the float, or independence of the density increment of solutions and the temperature.

### Acknowledgment

The authors wish to express their indebtedness to G. N. Lewis and R. T. Macdonald, who first used the flotation temperature method in this laboratory and out of whose technique the present work has developed. They also wish to thank Dale E. Callis, Merlin Reedy, and Forest J. Watson for their technical contributions, the Works Progress Administration (OP-465-03-3-147) for clerical and mechanical assistance, and the National Research Council for a grant made to the senior author for purchase of materials used in the study of heavy water.

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RECEIVED October 4, 1938. Mr. Longtin is Shell Fellow in Chemistry.



# Spectrographic Microdetermination of Copper

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THE need for a precise method for determining small proportions of copper in agricultural materials has led to the study of a spectrographic procedure. The advantages of spectrographic analysis over chemical analysis in speed and sensitivity are well known and in the method described below it has the additional advantage of eliminating all reagents except one. Microchemical methods for copper usually involve solution of the sample, one or more precipitations, and various other manipulations which increase the possibility of contamination with copper or of an appreciable loss of copper, when very small proportions are concerned. The procedure described here was designed to eliminate these manipulations in so far as possible.

There have been many determinations of copper with the spectrograph. Among those who have worked with biological materials are Gerlach and his co-workers (4, 5, 9), van Eyk (1), and Ramage and his co-workers (2, 10), who have used the following elements as internal standards in one or more of their studies: cobalt, molybdenum, silver, sodium, and tin. Either tin or cadmium is used as the internal standard in the procedure described here.

Langstroth and McRae (7) have pointed out that a desirable internal standard element should behave in the discharge very much like the element being determined and that the two should have as nearly as possible the same ionization potential. When copper lines 3247 and 3273 are being used, tin line 3262 is convenient, and in addition tin has other characteristics which make its use as an internal standard appropriate (see Table I).

TABLE I. INTERNAL STANDARDS

Element	Ionization Potential e-volts	Boiling Point ° C.	Wave Length Å.
Cu	7.68	2310	3247
Sn	7.30	2270	3273
Cd	8.96	767	3262

Tin and copper have boiling points very nearly the same, and this should contribute to a similarity of behavior in the arc discharge, and hence increase the precision of the determination. Occasionally, however, tin is detected in the sample in the qualitative spectrographic analysis which is always made first; in this event, another internal standard must be chosen, which in this study has been cadmium. Table I indicates that cadmium is not as satisfactory as tin as an internal standard for the determination of copper, at least with regard to the characteristics discussed above.

## Procedure

A large quartz Littrow spectrograph and nonrecording microphotometer have been used here, and essentially the internal standard procedure of Nitchie and Standen (8) has been followed. The magnified image of the direct current arc source (220 volts, graphite electrodes, 10 amperes) was focused on the slit of the spectrograph with a condensing lens. The arc was always maintained until the sample was completely volatilized.

Since the purest commercial graphite electrodes available frequently contain detectable copper, all electrodes have been purified, following the solvent purification procedure of Standen and Kovach (11). As all c. p. chemicals examined at this laboratory have contained spectrographically detect-

able copper, some purification is necessary before a base mixture for the calibration curve can be prepared. This has been accomplished by the use of the basic magnesium carbonate procedure as proposed by Steinberg (12). As many as ten recrystallizations did not remove copper as effectively as one treatment with magnesium carbonate.

The calibration curve was prepared by making up a base mixture of purified salts which approximated in its composition the proportions of the macroconstituents known to occur in the material to be analyzed. For example, a base mixture for the analysis of orange leaves would contain 40 grams of calcium carbonate, 2 grams of magnesium oxide, 6 grams of potassium sulfate, and 2 grams of sodium chloride. This mixture approximates the proportions as given by Kelley and Cummins (6) as shown in Table II.

TABLE II. BASE MIXTURES

	Kelley and Cummins' Data %	Synthetic Mixture %
Calcium	31.4	32.0
Magnesium	1.73	2.4
Potassium	6.40	5.4
Sodium	0.78	1.6
Sulfur	0.97	2.2
Chlorine	0.95	2.4
Carbonate <sup>a</sup>	50.65	48.0

<sup>a</sup> Calculated (cf. Gaddum, 3).

To weighed portions of the mixture (carefully homogenized) equal volumes of the standard tin solution and known volumes of a standard copper solution were added to give various standards over the range of concentrations (in this study 0.001 to 0.1 per cent) occurring in the material to be analyzed. The standards were dried, carefully homogenized in an agate mortar, and spectrographed. Twenty spectrograms were made of each standard; these were photometered, the average ratios of the copper-tin densities were determined, and a calibration curve was plotted on semilogarithmic paper with ratios as abscissa and concentration as ordinate.

Samples were ashed at 450° C., the ash was homogenized, and to weighed portions was added tin solution equivalent in volume to that added to the standards. These were dried, homogenized, spectrographed in quintuplicate, and photometered exactly as in the case of the standards.

## Precision and Accuracy

Factors affecting precision are nonuniformity of the sample, contamination, variation of exposure conditions (wandering of the arc, change of line voltage), photometric errors, and perhaps others. Every effort has been made to reduce the effects of these variables. Solutions of the samples would, no doubt, increase the precision, but at the same time would introduce unnecessary manipulation and the possibility of contamination with acids; with the precision required this is an unnecessary risk.

As a measure of the precision of this procedure, the probable error of the mean result has been calculated for a large number of samples which were analyzed in quintuplicate. In general, this was found to be about 5 or 6 per cent, although it was sometimes less. For example, in one set of 22 samples, the greatest probable error was 9.6 per cent of the mean, and the smallest 1.1 per cent, with an average of 4.5 per cent.

Factors affecting the accuracy are incomplete burning, influence of varying major constituents on the volatility and "excitability" of the copper and internal standard atoms, and perhaps others. In this study, the sample has always been completely burned, and, since standards are prepared which simulate approximately the composition of the unknowns, the

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influence of this factor is minimized. Langstroth and McRae (7) advocate the use of a spectroscopic buffer that will prevent reasonable variations in the extraneous composition of the samples from materially altering the transport phenomena. No spectroscopic buffer has been employed in this study, but its use presents interesting possibilities. It has been found here that when a calibration curve is prepared with a base material consisting, for example, of potassium chloride only, the slope is appreciably different from that of the calibration curve prepared with a base mixture containing calcium, magnesium, sodium, and potassium in the proportions indicated above for a representative orange leaf ash. This effect is more pronounced with cadmium than with tin as the internal standard. Therefore, plant samples containing large proportions of potassium may require a different calibration curve from those containing large proportions of calcium. The use of a spectroscopic buffer may obviate this difficulty.

### Discussion

This method may readily be extended to include both larger and smaller proportions of copper. The lower limit of spectrographic detectability of copper is less than 0.0001 per cent, and there is no upper limit. Above 0.1 per cent it would probably become desirable to utilize other copper lines than those used here, since their extreme sensitivity gives a plate blackening too great for convenient measurement.

The use of solutions of the samples has other objections than the one mentioned above. Of particular importance is the retention of copper in the insoluble residue. In addition, when solutions are dried on graphite electrodes, there is always some penetration, making it difficult to determine when the sample is completely volatilized. This penetration has been prevented by some workers by treating the elec-

trodes with kerosene or paraffin, but it has been found that this introduces some copper contamination.

### Acknowledgment

The author is indebted to Earle Peterson, R. C. Hughes, and L. L. Rusoff for assistance in the laboratory.

### Summary

A procedure is described for the quantitative spectrographic determination of copper in biological materials in the range 0.001 to 0.1 per cent by direct arcing of the ash. The probable error of the method is about 5 per cent.

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## A Simplified Method of Preparing Microscopic Glass Spheres

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WELL-defined microscopic spheres of glass (and similar high-melting substances) would be of considerable value for certain physico-chemical experiments if they could be prepared conveniently, but such material is not available commercially.

Sklarew (2) described in 1934 a method by which microscopic glass spheres may be produced by blowing glass powder through a blast lamp into a white-hot heat chamber which is connected to a steel pipe 300 cm. long and 90 cm. wide, leading to a 180 × 180 × 180 cm. cardboard settling chamber. The space required for this arrangement is not always available however, and the method is not very efficient as far as the quality of the product is concerned, many particles retaining more or less irregular shapes.

An attempt to use Sklarew's method in a moderately sized apparatus failed: It was difficult to keep the whole system sufficiently clean and the smallest particles, in which the author was most interested, did not settle down and thus were lost.

The method described below was finally found satisfactory for preparing the microscopic glass spheres needed for certain model experiments on colloids, adhesion experiments (now in

progress) using Buzágh's method (1), but using geometrically well-defined bodies instead of irregularly shaped ones.

The underlying idea can easily be gathered from Figure 1.

Oxygen is passed through a moderately sized glass bottle, A, containing some glass powder. A suitable orifice, B, and, if necessary, a slight agitation of the bottle cause the oxygen stream to be loaded with glass powder. The oxygen may be passed through a small settling chamber, C, before reaching the torch, E, through the rubber tubing, D. Gas is fed to the torch through a side arm. The flame originating at the orifice, F, is directed by hand against the surface of the water which fills the dish, G, up to the rim.

The particles carried with the oxygen pass through the flame in which they are molten, forming spheres. These spheres are thrown into the water, probably by centrifugal forces originating in the curvature of the flame when it strikes the water surface.

On microscopic examination, the particles are seen to be perfect spheres, entirely independent of each other, the smaller ones, of course, showing vivid Brownian movement. Among thousands of particles usually not a single imperfect sphere is found. They seem, except perhaps for the very biggest ones prepared thus far, free from internal strain, when tested microscopically between crossed Nicol prisms.

The whole arrangement is so simple that usually the first attempt will be successful, if a few precautions are taken.

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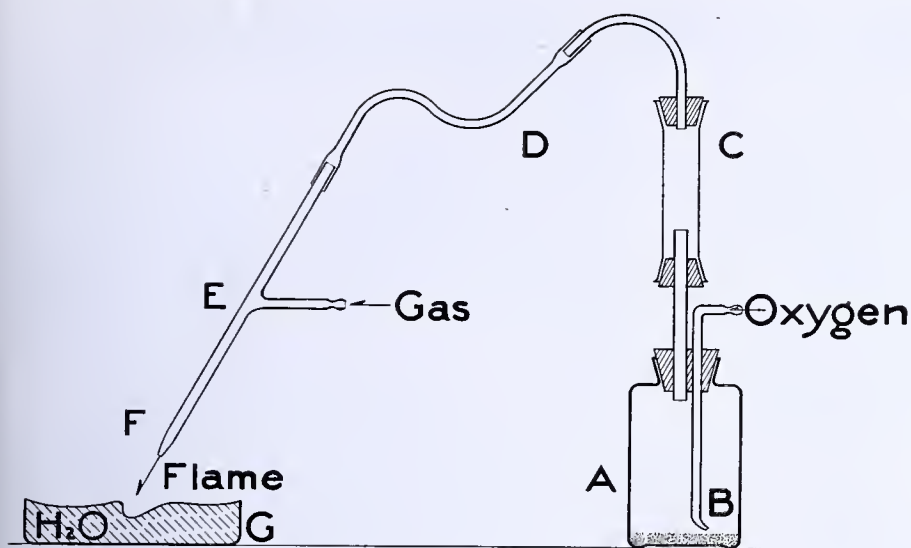


FIGURE 1. DIAGRAM OF APPARATUS

The gas and oxygen streams should be steady and properly adjusted; the quantity of glass powder carried by the oxygen should not be excessive and should be carried along uniformly and steadily. Thick-walled rubber tubing with a narrow bore should be used to secure high gas velocities; wider and thin-walled tubes lead to the formation of glass powder deposits owing to low oxygen velocities or kinks. Such deposits have a tendency to be blown out suddenly; then an excessive quantity of particles passes through the flame simultaneously and is not melted properly.

All containers, rubber tubes, etc., should be dry, and the glass powder should be carefully dried at increased temperature. If everything is dry each glass particle forms a single independent glass sphere; if the particles stick together because of moisture, these aggregates melt as units, forming big spheres that sometimes contain air bubbles.

Several commercial hand torches proved useful, particularly the type where the oxygen stream (carrying the powder) emerges at the orifice surrounded by a gas stream (Figure 2, upper). To avoid abrasion of metal by the sharp edges of the powder, the author used a simple quartz-glass torch (Figure 2, lower) to which a Pyrex glass tubing was fixed in the position indicated, below the torch, its constricted end being under the orifice of the torch a few millimeters back of it. Through the Pyrex tube some gas was fed, in order to surround the torch flame with combustible gas. In this manner every particle was sure to travel through a hot zone. Without this precaution, a few particles might occasionally slip through, without being melted completely.

The size and stiffness of the flame should be adjusted to the size and the melting point of the particles. A flame length of 5 to 10 cm. is sufficient for glass particles below  $10\mu$  diameter, but a hydrogen flame must be used for Pyrex. Small dishes—e. g., crystallizing—are suitable containers for the water.

The lower limit of particle size to which the method may be applied lies below that of microscopic visibility; the upper limit is probably determined by the flame size and the ability of the oxygen stream to carry big particles. Thus far the method has worked equally well with particles from below  $0.5\mu$  up to  $50\mu$  diameter, no attempt being made to apply it to bigger particles.

It is advisable to prepare many small lots instead of one large one because of the possible appearance of nonspherical particles due to the sudden discharge of deposits, as mentioned above. Each small lot is examined microscopically before it is mixed with the others.

The use of hydrogen prevents the dissolution of carbon

dioxide (and other impurities) in the water. Removal of such impurities can always easily be accomplished by repeated centrifuging out and redispersing of the particles in distilled water.

The simplicity of the method described allows in most cases the use of glass spheres prepared shortly beforehand, so that the time for a possible interaction between the glass and the water becomes greatly reduced. Even with soft glass such an interaction seems to be much less serious than might be expected—several samples of glass spheres prepared from soft glass (Williams and Hopkins, London, England) kept for a period of more than 2 years in water and aqueous solutions showed no detectable change, except that the distilled water showed a weakly alkaline reaction. But, of course, the particles are perfect spheres, absolutely independent of each other and showing lively Brownian movement when stirred up

by shaking. When considering the possibility of a chemical interaction between the spheres and the water, one must always remember that one is dealing with smooth surfaces, probably rather free from microfissures as compared with the original glass powder.

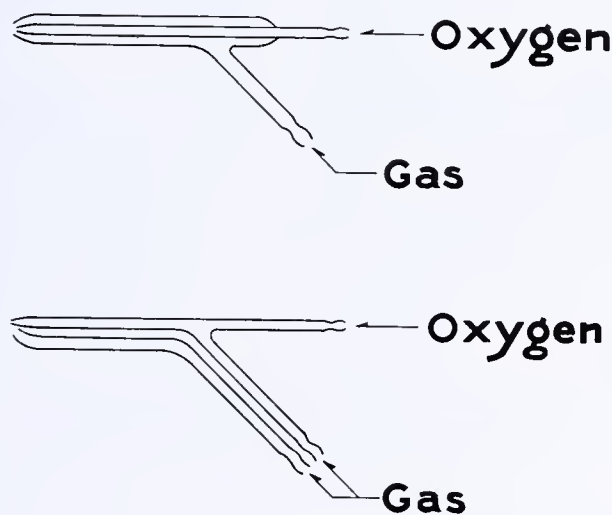


FIGURE 2. TORCHES

Though in the author's opinion the interaction between glass and water is not likely to go so far as to be a seriously disturbing factor when experimenting with the spheres, it is advisable to use freshly prepared spheres of resistant glass—e. g., Pyrex—or if possible of quartz.

An occasional attempt to prepare quartz spheres in a hydrogen-oxygen flame was not altogether successful; only the smallest particles were melted, often forming imperfect spheres. But there is no doubt that a more suitable torch and a bigger flame, or still better an acetylene-oxygen flame, would yield satisfactory results with quartz.

#### Acknowledgment

The author is greatly indebted to R. Bradfield, head of the Department of Agronomy, for generous hospitality in his department.

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# A New Apparatus for Microsublimation

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THE term sublimation describes the transition of a substance between its vapor and solid states without passage through the intermediate liquid state. If on raising the temperature of a solid substance the vapor pressure reaches 760 mm. before the fusion point is attained, the substance will sublime when heated in an open vessel under atmospheric pressure (iodine, ammonium chloride). Even if a substance has its triple point below 760 mm., it can be made to undergo true sublimation by heating *in vacuo*.

Where sublimation is feasible, it is frequently a useful technique in analysis, particularly in microanalysis. In a suitable apparatus separations can be effected on microsamples, and it is often possible to produce sublimate that are readily identifiable under the microscope by their crystal form and habit. In synthetic work sublimation has been found useful in the purification of materials. In the authors' laboratory the apparatus to be described has also proved convenient for the separation, by simple distillation, of the volatile and condensable components of minute samples—e. g., dust particles. In such cases the condensate takes the form of liquid droplets or amorphous or imperfectly crystalline masses, or a mixture of these.

The essential requirement for sublimation is a chamber so divided that a temperature difference can be maintained between two surfaces, on the warmer of which is placed the material to be sublimed. This temperature difference,  $\Delta\theta$ , will raise the pressure of the vapor in equilibrium with the solid by an amount  $\Delta p$ . The molecules leave the specimen surface, therefore, under a pressure  $p + \Delta p$  but are returned from the cooled sublimate at a pressure  $p$ , with the net result that material is transferred from the warmer to the cooler surface at a rate proportional to  $\Delta p$ . If  $\theta$  be kept below the fusion point of the substance, a solid condensate will always form and crystalline deposits usually result, since they are produced by the addition of molecules directly from the vapor state. Since for solids in general the  $p$ - $\theta$  relationship is not linear, one should, for maximum speed of sublimation, operate at the steepest portion of the  $p$ - $\theta$  curve. The distance separating the hot and cold surfaces should be as small as practicable, since the speed of transfer is naturally affected by molecular collisions occurring in this space. These collisions can also be reduced by evacuating the sublimation chamber. It will be obvious also that heavy molecules will be transferred more slowly than lighter ones, since the velocity of molecules in a vapor is inversely proportional to their molecular weight.

Various methods have been used in carrying out microsublimation. For the simplest qualitative purposes the material may be heated on a microscope slide and condensed on a second slide held immediately above and cooled by a drop of water placed on its upper surface. Lack of temperature control and incomplete recovery of the volatilized material are obvious disadvantages of the method. Improvements consist in placing the slide on a heated aluminum block provided with a thermometer, a glass ring separating the two slides.

When the sublimation is to be continued for longer periods, however, and under more carefully controlled conditions, more permanent arrangements are desirable, which provide for continuous cooling by water or air circulation as well as for evacuation of the sublimation space.

With the limitations of existing devices in mind, an at-

tempt was made to construct one which would combine, to the greatest practicable extent, the best features of each, together with original improvements designed to meet existing needs.

## Apparatus

The apparatus consists essentially of a cylindrical metal heating block, surmounted by a cooling block of the same diameter. The blocks are maintained in coaxial alignment by a pair of guide rods over which the upper block slides. A glass ring, ground into grooves in the opposing faces of the blocks, separates them. Water or air, circulating through the upper block, cools the glass slip which receives the sublimate. The sublimation chamber is removable and fits into a plunger mechanism in the heater block. A spring, acting against this plunger, forces the chamber up against the cooled glass slip. Details are given in Figure 1.

The Duralumin heating block, *A*, is spool-shaped to accommodate the heater winding, *Z*, of Nichrome wire. This winding is center tapped and the two sections may be connected in series or parallel, giving two heat ranges. At the center of the block an appropriately shaped well, *D*, accommodates a snugly fitting plunger, *E*, also of Duralumin. The main body of the plunger is bored out to form a receptacle for holding the sublimation cup, *F*. Proper alignment of the plunger and well surfaces, necessary for smooth movement, is maintained by a rod extension which fits the lower, narrowed portion of the well. A light helical spring, *S*, seated in a recessed portion of this lower well serves to force the plunger upward against the cooling block.

The interchangeable sublimation cups are of standard outside dimensions but have a variety of inside shapes and sizes such as are shown in details *F*<sub>1</sub>-*F*<sub>4</sub>, suited to different uses. The cup is about 0.5 mm. higher than the accommodating receptacle in the plunger. This prevents the latter from touching the cooling unit, which would result in an undesirable transfer of heat with consequent loss of efficiency. The well is of sufficient depth to permit pressing the plunger completely into the block. Fine grooves, filed longitudinally into the sliding surface of the plunger, permit passage of air to and from the well. From points diametrically opposite on the upper spool flange, two 0.6-cm. (0.25-inch) holes, *U*, are drilled to a depth within 1 or 2 mm. of the well. Beyond the block, they are continued in the form of sleeves, about 2 cm. in length. One of these holes accommodates the thermometer for measuring the block temperature. The other holds the thermometer unit.

The vertical guide rods, *I*, which hold the upper block in alignment, are set in the upper face of the heater block at points 90° from the thermometer and thermoregulator holes and about 5 mm. from the edge. These rods are fluted to reduce heat conduction. The upper face of the heater block also contains a circular groove, *J*, 2 mm. deep and 3 mm. in breadth. The cooling block has an identical groove cut in its lower face. The glass ring, *L*, which separates the blocks has its edges ground into these grooves. If the apparatus is to stand on the table, short brass rods may be set into the bottom of the block to provide feet. For panel mounting, the block is supported by three 0.47-cm. (0.19-inch) steel rods threaded into the spool flanges at right angles to the thermometer and regulator. Two of these rods enter the top flange, and one enters the bottom. The metal surface of the spool is covered with thin asbestos paper, the heater coils are then put in place, and the space between the flanges is filled with Alundum cement. The heater coil leads are brought out through three holes in the bottom flange, each fitted with a ceramic insulating bushing.

The cooling block, *B*, is constructed of brass. On its lower face a central cylindrical extension, *W*, carries the metal slide, *C*, on which the glass slip is held by a tiny spring clip, *T*. The slide projects slightly above the retaining slot to prevent fouling the edges of the glass slip when it is removed from the block as well as to reduce unnecessary heat transmission. A stop pin, *Y*,



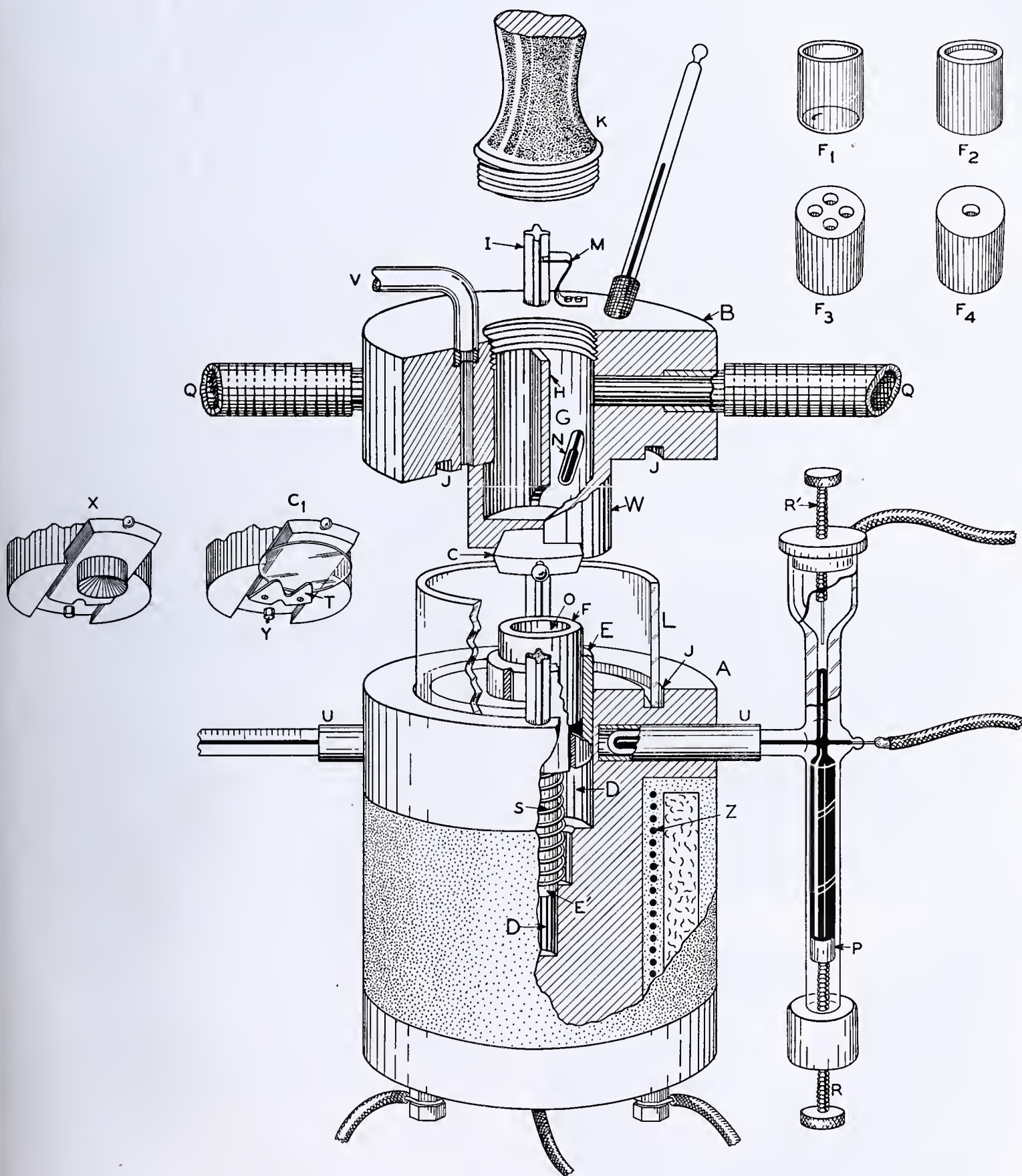


FIGURE 1. DIAGRAM OF SUBLIMATION APPARATUS SHOWING DETAILS OF CONSTRUCTION



fitting a small recess at the back end of the slide, prevents slipping past the center point. The slide may therefore be taken out for inspection and put back with assurance that the glass slip which it carries will be returned to its original position relative to the sublimation cup. A small knob at the front end of the slide facilitates its removal. The whole arrangement is shown in greater detail in *C*<sub>1</sub>.

A well, *G*, is drilled from the top of the block, down into the cylindrical extension, *W*, to within 2 mm. of the bottom of the slide slot. Near the top of the block at points diametrically opposite, holes are drilled which communicate with the well. Outwardly each of these terminates in a 2.5-cm. (1-inch) length of 0.6-cm. (0.25-inch) tubing for hose connection *Q*. Water or air circulating through these tubes is forced to traverse the full depth of the well to obtain maximum cooling at the bottom, by means of a metal baffle, *H*, fitting tightly against its walls in a plane at right angles to the axis of the inlet and outlet tubes. A V-shaped notch at the lower end of this baffle allows passage of the cooling fluid. The top of the well is closed by the plug-shaped end of a Bakelite or hard-rubber handle, *K*, threaded into it. A rubber washer between the bottom of this handle and the edges of the baffle seals off the two sections of the well. A 0.6-cm. (0.25-inch) hole, *N*, is drilled diagonally from the top face of the block into the lower portion of the well on the exit side of the baffle. This accommodates a thermometer for measuring the temperature of the outflowing cooling fluid. At the top of this hole, a small recess permits the insertion of a rubber ring, making a water-tight fitting for the thermometer. A small hole is also drilled downward through the block to a point just inside the circular groove on the lower face. On the upper face, this hole terminates in a tubular hose connection, *V*, that serves to evacuate the space enclosed by the glass ring when the blocks are brought together.

Holes near the edge of the block, 90° from the inlet and outlet tubes, are provided for the guide rods, and should obviously be placed so that the blocks are coaxially aligned. A spring catch, *M*, which snaps into a notch at the top of one of the guide rods is

mounted on the upper face of the cooling block and serves to hold the blocks apart during preparatory manipulations. The glass separating ring, *L*, should be of heavy-walled Pyrex tubing with the ends ground to parallel planes. Its height is such that when ground into the grooves, the cooling slide is held within 2 mm. of the heater-block face. Grinding in should be finished with 600-mesh Carborundum and should continue until leakage is very slight when connected to the suction line. It should be possible to maintain a 76-cm. (30-inch) vacuum with the average pump.

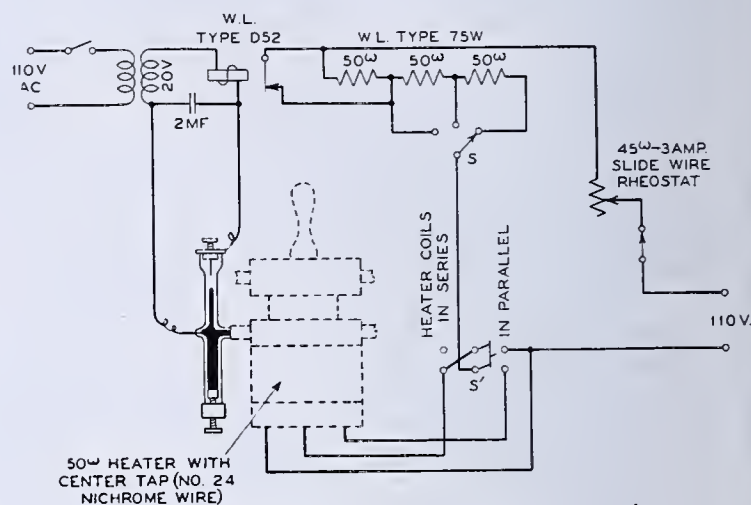


FIGURE 3. WIRING DIAGRAM

The thermoregulator used in this assembly obviously must be small and yet constructed to cover a wide range of temperatures. Such range cannot be obtained through raising or lowering of the contact point. It is necessary to introduce or to remove mercury from the expanding column. As may be seen in the drawing, this is done by providing a reservoir with ground-in glass plunger similar to that used in hypodermic syringes. The capacity of the reservoir is controlled by an aluminum screw, *R*, of large diameter, acting against the plunger. This reservoir is joined directly to a small L-shaped regulator. Adjustment of the contact level by the knurled screw, *R'*, at the top provides the fine adjustment.

Use of the apparatus is extremely simple. The cooling block is raised until the catch engages the notch in the guide rod. The glass ring is removed and the slide withdrawn. A thoroughly clean microscope cover slip is placed on the slide, with its edge under the spring clip and its center approximately at the center of the slide. (A tiny punch mark on the slide to denote the axis of the assembly is helpful.) The material is placed in one of the sublimation cups and this, in turn, placed in the plunger. The glass ring is replaced, care being taken to see that no dust has fallen into the groove. The cooling block is lowered until it rests on the glass ring. Rotating in alternate directions with the fingers when the suction is turned on helps to seat the ring in the grooves. Current and cooling water or air are then turned on.

The process is stopped by simply turning off the suction and raising the cooling block. The plunger rises out of the block with the sublimation cup and the temperature quickly drops. By removing the plunger with forceps and replacing the cup a second sublimation may be started without cooling the block.

### Discussion

The interchangeable cups provide convenient adaptation to varying types of specimens. The capacity of the subliming chamber may be thus reduced to a few cubic millimeters when dust particles or single crystals are dealt with. On the other hand, it may be large enough to accommodate small mechanical parts, the surface of which is to be examined for traces of waxy or oily matter as well as for volatile inorganic substances such as mercury or ammonium chloride.

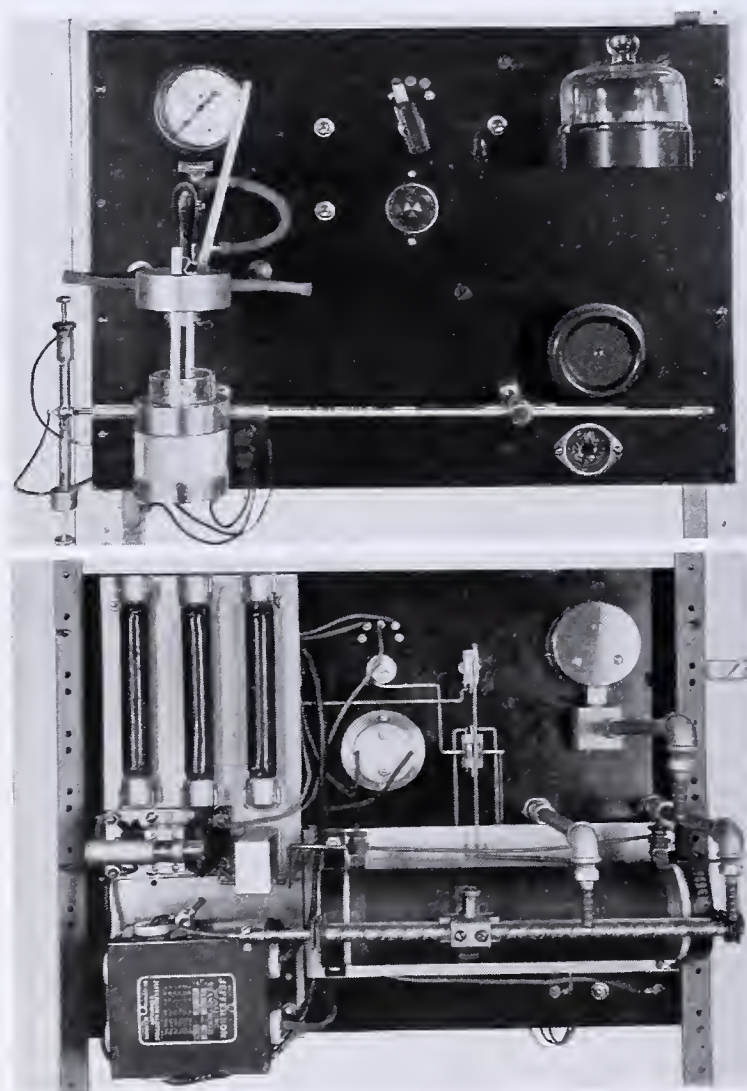


FIGURE 2. COMPLETE SUBLIMATION APPARATUS SHOWING DETAILS OF PANEL MOUNTING



Microdistillation of high-boiling substances under reduced pressure can also be carried out satisfactorily. When the quantity distilled is very small, or the viscosity of the distillate is high so that coalescence of the deposited droplets is prevented, the distillate is received on the cooled cover glass, as in sublimation. Larger quantities of more fluid substances are condensed on the arrangement shown in detail X (Figure 1). Here the regular cooling slide which holds the cover glass is replaced by one of silver which carries a cylindrical process on its lower face. The end of this cylinder is bored out to form a funnel-shaped reservoir inverted over the rising vapors which condense in it. Plating with gold or platinum affords protection from corrosive products. When a metal cup is used, a ring of glass or ceramic material interposed between its edge and the condenser slide reduces unnecessary heat transfer. Liquids not too viscous may be concentrated in the narrow "stem" of the funnel by centrifuging. From this they may be withdrawn with capillary tubes.

If the edges of the glass ring enclosing the evacuated space between the blocks are in perfectly parallel planes and grinding into the grooves is done carefully, little leakage of air occurs. However, even if this were considerable, it still would have little disturbing effect on the material in the sublimation cup, since communication is established only through leakage between the cup edge and the cover slip. Vapors tending to pass outward must therefore traverse the cooled surface of the latter and condense. As a result, quantitative recovery is closely approached, even in vacuum sublimation. Attainment of this goal is also furthered by the sharp temperature gradient maintained between the cup walls and the receiving slip. This facilitates the concentration of all the sublimate on a sharply defined area with practically no loss due to partial condensation on zones of intermediate temperature.

Alignment of the cooling block on guide rods and retention of the glass slip by a removable metal slide have distinct advantages. When the upper unit is raised, the slip and sublimate which it contains are lifted from the cup with a purely vertical motion, without interruption of the cooling. In this way smearing of the deposit and accidental volatilization of sublimate through leaving the uncooled slip, even for a short time, on the heated cup are both entirely prevented. When the weight of the cooling block is removed, the sublimation cup is forced out of the heater block by the spring acting on the plunger. Volatilization of material is thus arrested. This feature, combined with the slide, permitting quick removal of the glass slip, simplifies the problem of changing the slips at regular intervals when fractional sublimation or distillation is desired. No cooling of the heater block is necessary.

The use of metal for construction of the essential parts of the apparatus makes possible a more compact and less fragile unit and permits higher operating temperatures. The thermostatically controlled electrical heating makes it practicable to carry on sublimation or distillation over long periods of time with accurate control. The cooling of the receiving slip can be regulated by varying the rate of flow of the water or air through the upper block. The thermometer on the outgoing side of the baffle indicates the heat transferred.

The writers have found it convenient to mount the apparatus, together with electrical equipment, pressure gage, water outlets, etc., on a Bakelite panel which may be fastened to the wall or to a suitable rack, thus conserving table space. A complete portable unit is thereby provided, and the necessity of making flimsy connections between scattered pieces of equipment is eliminated. The photographs in Figure 2 show such an assembly. The electrical circuit is given in Figure 3.

It is the authors' belief that an extension of the idea of panel mounting to other forms of microchemical equipment would distinctly improve both the efficiency and appearance of the laboratory.

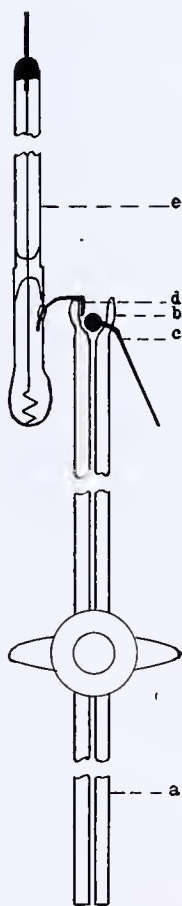
RECEIVED September 30, 1938. Presented before the Microchemical Section at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

## Hydrogen Electrode for pH Microdeterminations

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THE apparatus illustrated has been found useful in this laboratory for determining pH on volumes ranging from 5 to 60 cu. mm., having the advantages (and disadvantages) of the hydrogen electrode but being more satisfactory with small volumes.



The electrode is constructed by cutting off the ends of a 1-mm. bore capillary stopcock, leaving approximately 8 cm. on each side of the cock. One end, *b*, is widened into a cup-shaped cell capable of holding a maximum of 0.1 ml. A small bead is formed on the end of a 3-cm. length of No. 20 platinum wire, flattened to a thin disk (1.5-mm. radius) and sealed in position as shown, *c*, with the thin edge in line with the capillary bore.

As calomel half cell the inner element, *e*, of the E. H. Sargent calomel electrode assembly, S-30,445, may be used without modification.

A satisfactory bridge is formed by soaking a piece of No. 50 cotton thread in saturated potassium chloride solution and then placing as shown, *d*. Natural and artificial silks, ramie, etc., are also satisfactory.

The electrode is plated by immersing the cell end in the ordinary plating (*I*) solutions and connecting as cathode. The electrode is washed by immersing in distilled water, the residual droplets being blown out by passing purified hydrogen through *a*.

After thorough cleansing, the electrode is inverted and connected to the calomel half cell as shown. If the cock is closed, when the solution is introduced into the cell by a micropipet the trapped gas in the capillary prevents the solution from dropping out of the cell. With a slight hydrogen pressure on *a*, turning the stopcock permits the gas to pass through the cell and form small bubbles, which are blown up to the mouth of the cell, coming in contact with both the blacked platinum disk and thread bridge. At the mouth the bubble breaks, the solution immediately flowing down the inside of the cell to the neck and forming a new bubble. Best results have been obtained when approximately 30 bubbles per minute formed. Equilibrium is reached very rapidly.

To determine the accuracy of this cell buffer solutions ranging in pH from 2.4 to 10.2 (in steps of 0.4 pH) were prepared and studied. The e. m. f. values recorded, using a type K-2 potentiometer, checked those obtained using a Hildebrand-type electrode on larger volumes of the same solutions.

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RECEIVED November 7, 1938.



# A Microdistillation Apparatus

## With Receiver for Distilling under Reduced Pressure

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An all-glass apparatus combining a receiver of new design with a microdistilling column for the distillation of high-boiling liquids is described. The receiver allows several fractions of the distillate to be collected without interrupting the pressure under which the distillation is performed.

Design and method of constructing the apparatus for 0.5 to 2.0 grams of material are given.

The apparatus is easily cleaned and assembled, and shortens the time required for a distillation.

SINCE their introduction in industrial laboratories, microdistillation procedures have constantly required improvements to reduce further the mechanical manipulations, thus broadening the field of application of some of the micromethods already familiar to industry.

Although several devices for microdistillation under reduced pressure (2, 3) have been reported, no attempt has been made to complete the distillation without interruption of the pressure under which the distillation is performed. This laboratory was confronted with the need for an apparatus for distilling small quantities of substituted benzene compounds. These compounds for the most part boiled at 225° to 325° C., and the apparatus here described seems an improvement justifying a communication at this time, although the work is still in progress.

### Design of Apparatus

The flask and column of the apparatus are similar to that of Clarke and Hermance (1). The design of the side-arm delivery tube and that of the receiver for collecting the distillate were perfected in this laboratory during the past 2 years. The flask has a greatly flattened bottom; the size may be varied to suit special conditions or particular liquids. When a thin layer of 30-mesh silicon carbide or clean sea sand is used in place of boiling chips, as is customary in macrodistillations, evaporation takes place without active ebullition, thus eliminating bumping. An extremely small holdup becomes necessary, and this requirement can be fulfilled by using a Vigreux column.

The internal projections made by punching indentations in the column act as baffles to arrest accidental spray and reduce the volume of the column to a minimum.

The receiver is constructed for easy removal of the fractions when the distillation is completed. The all-glass receiver has the advantage that no contamination from rubber stoppers is possible, and the desired amount of distillate can be estimated for each fraction before collecting the succeeding portion.

The apparatus shown in Figure 1, designed for volumes of 0.5 to 2.0 grams of material, is easily cleaned and assembled and relatively easy to manipulate. It has a holdup (weight of material in apparatus when the distilling flask has become dry) of approximately 0.08 to 0.12 gram of liquid, the column being 7 to 15 cm. in length and approximately 5 mm. in inside diameter. The receiver (Figure 1) contains small glass cups, each having a capacity of 0.10 ml. These cups are arranged in a circle of nine or more, so that each succeeding fraction distilled can be collected by rotating the entire receiver around joint *f*. The number of cups is variable with the thickness of the glass tubing used and the size of the glass joint, *m*. The details of the unassembled apparatus are shown in Figure 2. A condenser was not necessary for

most of the liquids distilled in this laboratory. When low-boiling liquids are distilled, the side arm *e* may be wrapped with a cloth containing powdered solid carbon dioxide.

### Constructional Details

The distilling flask, *a*, is a flat-bottomed bulb of 4-ml. capacity having neck with stopper to fit. The neck and stopper are made from a  $\frac{7}{25}$  ground joint. Onto the top of the flask is sealed a 6.5-mm. tube, *c*, which is approximately 0.75 mm. in wall thickness and contains as many internal projections (4 to 5 mm. from center to center) as is convenient. The column has an outside jacket, *d*, 15 mm. in outside diameter, evacuated with a mercury vapor pump. The jacket is wrapped with aluminum foil further to insulate column *c*.

A 5-mm. tube is sealed to the top of the column and bent downward to form side arm *e*. The lower end of the tube has a  $\frac{7}{25}$  glass joint to which is sealed a 5-mm. tubing, *g*. The latter is ground on a wheel to an angle, the long side being 9 mm. and the short side 4 mm. from the small end of the male part of the ground joint, *f*. To the long side of tube *g* is sealed a 1.0-mm. glass rod, tapering to 0.8 mm. The length of the glass rod varies with the distance the receiving cups, *j*, are placed from

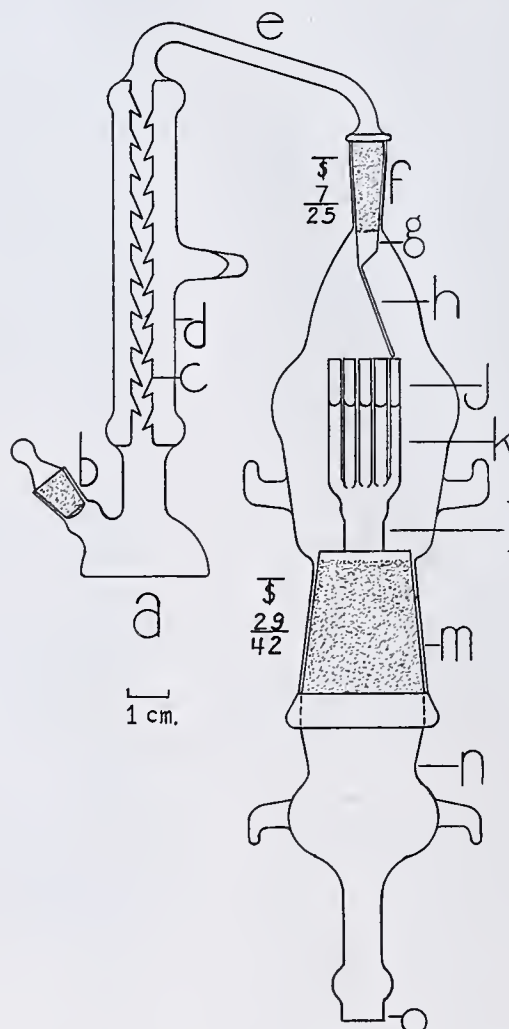


FIGURE 1. DIAGRAM OF APPARATUS





FIGURE 2. DETAILS OF UNASSEMBLED APPARATUS

the exit end of the side arm, the most convenient length being 225 to 290 mm.

Several different arrangements have been tried for conducting the drops of liquid from the side arm into the receiving cups, the one described above proving the most satisfactory. The only requirements for continuous transfer of the liquid from the side arm to the cups are: the glass rod, *h*, must be smoothly sealed to the lower end of the side arm with the end of the rod extending directly over the cups; and the apparatus must be entirely free from grease.

The receiving cups, *j*, for collecting the distillate are made from 4-mm. thin-walled glass tubing which is sealed to 4-mm. glass rod *k*. The rods with the cups are sealed to a 10-mm. glass rod, *l*, and the latter is made a part of the removal male glass joint, *n*. This latter operation is performed by closing the small end of the male joint and sealing the 10-mm. glass rod to the center of this closure. A 6-mm. hole (Figure 2) is then blown opposite this connection to permit evacuation of the apparatus by attaching tubing to vacuum pump at *o*.

The distilling flask is heated by means of an oil bath, which is stirred mechanically by a small air-driven stirrer. A thermometer in the oil bath is the only means of measuring the temperature.

A 1-mm. layer of clean sea sand or 30-mesh silicon carbide is placed on the bottom of the flask and the liquid is inserted with a pipet through neck *b*. The flask is connected to the receiver and the apparatus evacuated to the desired pressure. The temperature of the oil bath is then slowly raised until a steady reflux is maintained in the column. To do this it is necessary to adjust the temperature of the oil bath to  $\pm 1.0^\circ \text{C}$ . to permit only one or two small drops of the liquid to be distilled during 3 minutes. If a large amount of liquid is driven over, the column floods and the efficiency of the apparatus is impaired. A uniform reflux is essential for best results.

Arbitrary fractions are collected by rotating the receiver containing the glass cups around joint *f*, rather than at *m*, there being less resistance, especially when a high vacuum is maintained. When the distillation is complete, air is allowed to enter the apparatus at *o*, and the lower part of receiver *n* is removed. The refractive index, boiling point, and chemical analysis, if desired, are determined on the separate fractions by well-known micromethods.

The receiver described here has been used with the Vigreux-type column, and the column described by Craig for

high-boiling liquids. The latter was used in those cases where the liquid did not wet the glass surface. A short ground-glass joint was placed between the flat-bottomed flask and the column used by Craig to facilitate introduction of the resistance wire and the inner part of the column.

### Tests on a Synthetic Mixture

Although the apparatus described has been used primarily for determining the boiling range of organic liquids obtained in small amounts, actual tests on the separation of synthetic mixtures were made to be sure of the value of the apparatus.

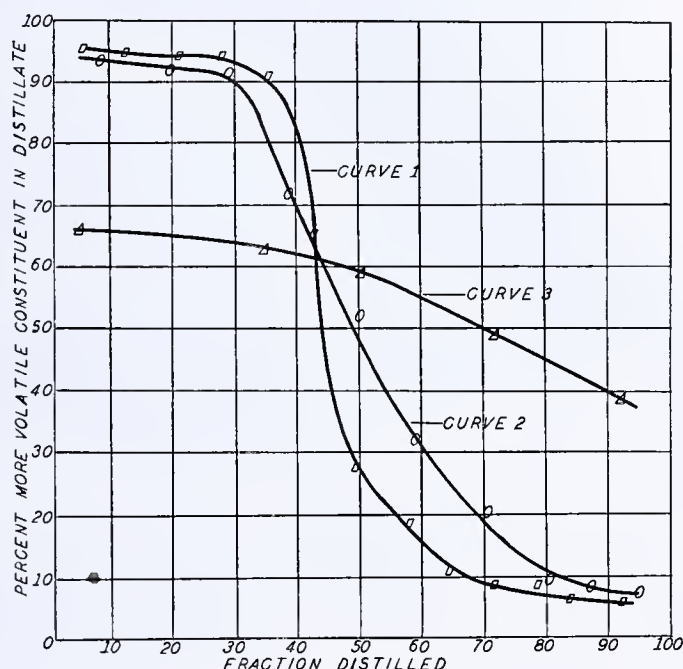


FIGURE 3. TESTS ON 50-50 MIXTURE OF ISOAMYL SALICYLATE AND CAPRYLIC ACID

- Separation obtained by Craig's column
- Vigreux column with evacuated jacket and receiver
- △ Vigreux column without evacuated jacket but with receiver

The curves (Figure 3) represent graphically a comparison of the results obtained with a 50-50 mixture (per cent by weight) of caprylic acid and isoamyl salicylate. The analyses were made by the refractive index method. Curve 1 represents the separation given by the column described by Craig but without the receiver. Curve 2 is the separation obtained with a 15-cm. column and the receiver as described in this paper. Curve 3 represents the results obtained with an apparatus similar to the one described, but without the evacuated jacket surrounding the Vigreux column. In each case 1 gram of the mixture was used and the distillation was done under 1-mm. pressure.

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RECEIVED September 26, 1938. Presented before the Microchemical Section at the 96th Meeting of the American Chemical Society, Milwaukee, Wis., September 5 to 9, 1938.





## THE METCALF RESEARCH LABORATORY AT BROWN UNIVERSITY

HARTLEY C. ECKSTROM  
Brown University, Providence, R. I.

THE new Metcalf Research Laboratory, the construction of which was made possible by a gift of half a million dollars from former Senator Jesse H. Metcalf, stands on the Brown Campus adjacent to the Jesse Metcalf Memorial Laboratory, a gift from Mr. Metcalf in 1922. The architecture of the new laboratory, like that of the older structure, is Georgian and harmonizes with other nearby buildings. In addition to the building, Mr. Metcalf's gift provides for much new research equipment and endowment for research.

The new laboratory is a three-story structure, with basement, having a length of 130 feet and a width of 48 feet. Its primary purpose is to provide research facilities for the staff and students of the Department of Chemistry. It also houses the laboratories of undergraduate physical chemistry and the combined libraries of the Departments of Chemistry, Physics, and Mathematics.

The arrangement of laboratories and service rooms will be evident from the floor plans. The corridor walls divide the building so that the laboratories on either side have a depth of 19 feet. The corridor ends at a transverse partition wall at the west side in order to provide some larger rooms, 30 × 45 feet, which may be used intact or divided suitably to meet the need for laboratories of unusual size and shape.

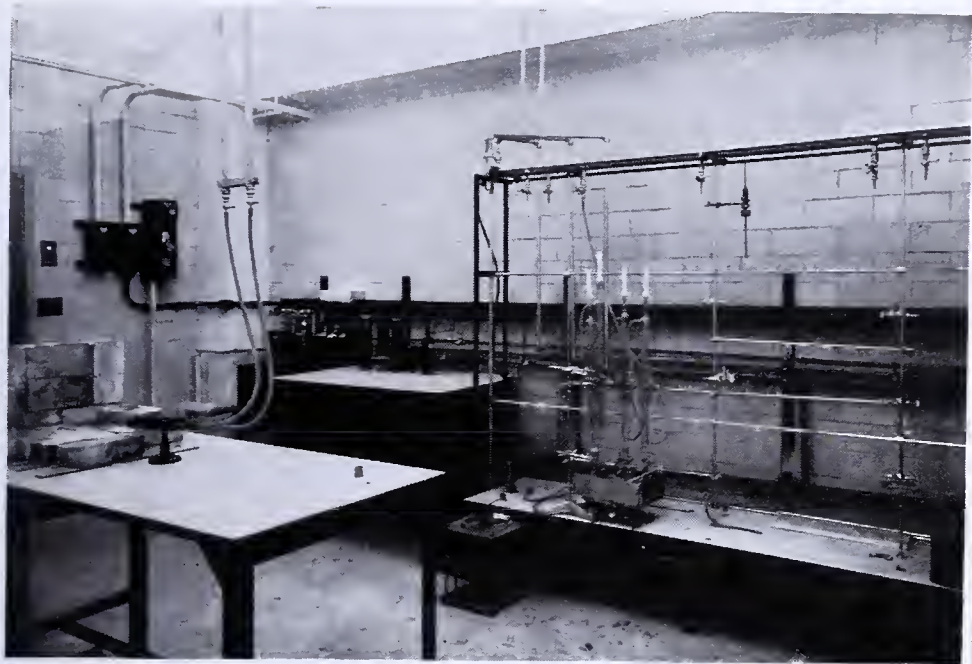
In the basement are laboratories for photochemical and spectroscopic research, the machine shop, generator and switchboard room, storerooms, and the air-conditioning unit. Undergraduate physical chemistry is provided with a large laboratory on the west end of the first floor, as well as several small laboratories, a dark room, and a storeroom. Except for one office, the remaining space on the first floor has been

divided into small laboratories, all equipped with light-tight blinds. On the second floor are located offices, a conference room, research rooms, and service rooms which include a storeroom, an instrument room, a balance room, and a conductance room. Altogether, there are twenty-two research laboratories capable of accommodating thirty-five laboratory workers very comfortably.

Numerous rooms are provided for special purposes; they include the microphotometer room, grating room, spark room, special spectroscopic laboratories, two darkrooms, and computing room. The combined chemistry, mathematics, and physics libraries are housed on the third floor, where there are two levels of stacks accommodating 60,000 volumes. In addition, there are a reading room, three offices, and a small conference room. Additional reading room is provided by means of carrells along the south and north walls at the end of the stacks. A small freight elevator connects all three floors and the basement. It is located next to the stock rooms, thus providing an easy means of transporting heavy equipment and stock from one floor to another.

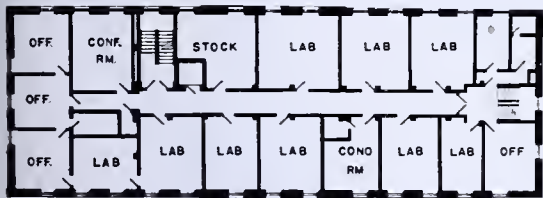
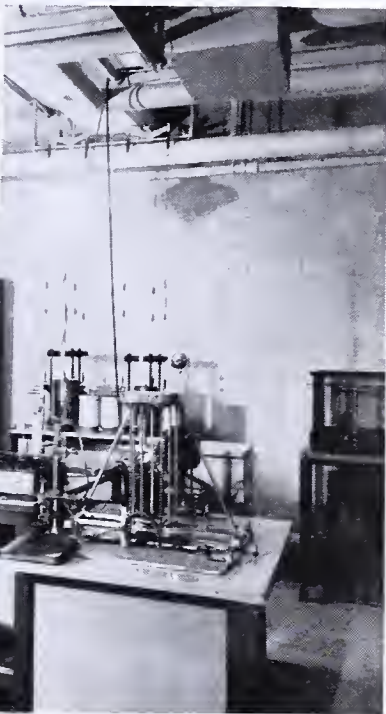
The entire building was designed so that it may easily be adapted to any type of research. The only permanent floor fixture in any laboratory is the sink. All sinks are Karcite and are provided with steam and steam mixers. All chemical desks and tables are constructed of steel with Transite tops and are portable. Around the walls of all laboratories, pipes for gas, water, and air are attached to racks by means of small brackets and a special pipe for water drainage is hung below these. This arrangement permits the moving of tables, desks, ammonia benches, and special apparatus to any



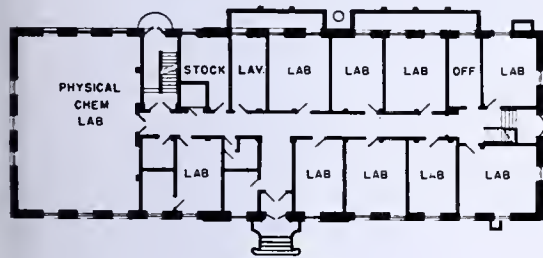


Above. LAYOUT OF  
LABORATORY 213

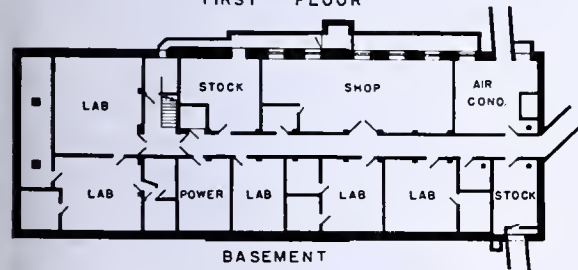
Below. . LAYOUT OF  
LABORATORY 5  
Setup of freezing point  
apparatus



SECNDND FLOOR



FIRST FLOOR



BASEMENT

FLOOR PLANS

part of a laboratory with the necessary services always available. All the services—water, gas, air, and steam—that supply a laboratory may be shut off in that laboratory, so that any necessary changes may be made in a laboratory without disrupting the work in any other part of the building. Since all pipes and electrical conduits are exposed, changes may be easily made.

Each laboratory is also provided with 110- and 220-volt alternating current, 110-volt direct current of 35 amperes capacity, and two special circuits with a carrying capacity up to 100 amperes. These circuits run directly to the switch-board in the basement. In all laboratories, the 110-volt alter-

nating current circuit is run along the walls in a 4 × 4 inch steel trough with hinged front, fastened to the wall racks above the pipes for water, gas, air, and drain. Whenever it becomes necessary to add other electrical services, the conductors may be laid in this trough. All laboratory circuits, except special circuits, are provided with individual circuit breakers. The special circuits terminate in safety switches. This, again, permits changes to be made in the wiring of any laboratory without inconvenience to workers in the rest of the building.

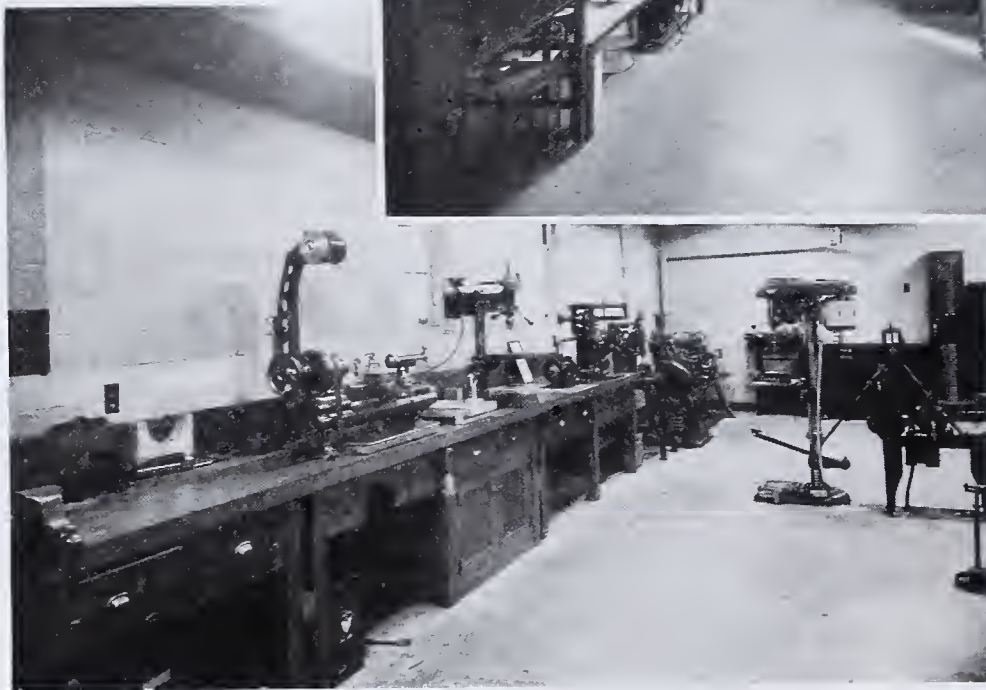
The photographs illustrate the flexibility of the arrangement adopted. The steel trough conduit, the water, gas, and air pipes, and the water drain are clearly visible. A unit of two circuit breakers and a special circuit safety switch is visible in Laboratory 213. The design and construction of the ammonia benches and the manner in which they are connected to the services may also be seen in Laboratories 204 and 213.

Since the building is fire-proof throughout, with the interior walls and facing of vitrified tile, it was necessary to provide an easy means of hanging pipes, conduits, and wires, and of suspending special apparatus, such as galvanometer suspensions. This was accomplished by means of ceiling inserts which are regularly spaced at 4-foot intervals in all laboratories, starting 1 foot from all walls. By means of special hangers, any type of apparatus or pipe may be readily hung without boring holes in either the walls or the ceiling. In Laboratory 213 the pipes for gas and air are run across the ceiling to the middle of the



*Right.* LAYOUT OF LABORATORY 204

New parallel high-resistance bridge and thermostat on right



*Left.* MACHINE SHOP

room for use with a blast lamp and two galvanometer suspensions and numerous wires are shown hung from the inserts in Laboratory 5.

The undergraduate physical chemistry laboratory and several other laboratories are equipped with hoods which are constructed of black composition stone with glass doors. Each hood is provided with a sink, and with water, gas, air, steam, and electrical services. The table tops in the hoods are removable, so that racks, similar to those of the ammonia benches, may be set up inside the hoods. Each hood is provided with an individual exhaust fan. All other laboratories are provided with ducts for fume ventilation. Not more than two laboratories are connected to one exhaust fan and all fans have a capacity of 900 cubic feet per minute. The ducts are constructed of Transite pipe. The fans are placed just under the roof, and each fan has its own exhaust to the atmosphere, so that there is no danger of a down draft returning the exhausted fumes to another laboratory.

Near the south wall in the basement of the building provision has been made for hanging a 110-foot absorption tube for spectroscopic work. On the west side, in the basement, a special thermally insulated room has been provided for a 21-foot grating which will be used with a modified Eagle mounting, and has been so arranged that the grating may be used in conjunction with the absorption tube. The machine shop, which is 50 feet long and 18 feet wide, provides ample facilities for machine work and apparatus construction required for research purposes. In one corner of the shop, a small student shop has been provided and equipped with a small lathe, drill

press, and other tools. The shop is lighted by means of mercury vapor lamps. Fume ventilation is provided by means of an open-faced hood. All machines are individually driven by means of three-phase motors. Since the basement laboratories have no windows, it was found necessary to air-condition the basement. The air-conditioning equipment has a capacity of 2,000 cubic feet per minute.

On the second floor, a special room has been fitted up for conductance work. In this laboratory is a shielded, sound-proof room which holds the bridge used for conductance measurements. Connected to the balance room is a thermally insulated room which is used to house a microbalance. The balance room itself is used only for special balances of high sensitivity; other balances are distributed in the various laboratories as needed.

Every effort has been made to ensure adequate lighting in all parts of the building. Each research laboratory, depending upon size, has from two to six ceiling fixtures, each of 350-watt capacity. In addition, a special ceiling receptacle with its own switch is provided to supply additional lights as required.

Each research laboratory is furnished with a chemical desk which has three drawers, plain tables, a glass-blowing table, an ammonia bench, a storage cabinet, a clothes locker, and a desk with lamp and chair and a bookcase. Each ammonia bench is furnished with gas, water, air, and electricity. The chemical desks are open underneath and have no lockers for storage; adequate storage space is provided in 72 × 36 × 18 inch cabinets.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Spectrographic Methods of Trace Analysis

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The field of application of spectrographic methods for the qualitative and quantitative analyses of materials for traces of metals and metalloids has been considerably enlarged in recent years by the development of improved technique. These methods have been applied to the analyses of heavy and organic chemicals, pharmaceuticals, and biological, geochemical, and metallurgical materials. The sensitivity and accuracy of these methods have been increased by the use of spectral sources of excitation particularly adapted to the analyses of different materials and by the use of well-tested means of photographic pho-

tometry. The following sources have been found to be appropriate for the indicated analyses: the high-voltage, alternating current arc for inorganic chemical products; the direct current arc for metallurgical specimens; the cathode layer of the direct current carbon arc for geochemical samples; the direct current condensed spark and the high-voltage, alternating current arc for organic chemical and biological materials.

The speed and adaptability of spectrographic methods have contributed materially to their usefulness for research and control analyses.

**S**PECTROGRAPHIC analysis of materials is based upon the fact that each chemical element in the vapor state, under suitable thermal or electrical excitation, emits radiation composed of characteristic wave lengths, or spectral lines. The wave lengths of the spectral lines emitted by each element are different from those emitted by any other element. This is the basis of qualitative analysis. The intensities of the spectral lines emitted by each element under controlled conditions of excitation are proportional to the concentration of that element in the specimen. This is the basis of quantitative analysis. The best quantitative analytical technique rests upon the experimental determination of the relationship between the concentration of a constituent of a specimen and the relative intensity of a pair of selected spectral lines, one of that constituent and the other of an internal standard element present in or introduced into the specimen in constant amount.

The emission spectrum, to which this paper is limited, is suitable for the detection and determination of the metallic and metalloid elements.

For the purposes of this paper a trace element will be defined as one contained in a concentration of less than 0.01 per cent in a specimen.

This method of analysis is particularly suitable for the determinations of ele-

ments present in trace amounts. Its principal advantages are:

1. The amount of sample required is extremely small; a few milligrams suffice in many cases for a complete quantitative analysis for the metallic constituents.
2. A minimum amount of chemical preparation of the sample for analysis is required. The simultaneous identification of the different elements, and the determination of their concentrations, may be made without previous chemical separations.
3. The sensitivity is very great. Most elements can be determined in concentrations down to 0.0001 or 0.001 per cent. In some matrices certain elements may be determined down to concentrations approaching 0.000001 per cent.
4. The precision and accuracy of analysis for elements occurring in concentrations of a few ten-thousandths to a few thousandths per cent are valuable, for in many instances this method provides the only practicable means of determination.
5. The rapidity of the method, where applicable, in general saves a considerable portion of the time and cost required for a chemical analysis.
6. A complete qualitative analysis of the specimen for its metallic constituents may ordinarily be made by inspection of the same spectrum which is used for the quantitative determination of one or more elements.
7. By the use of best technique the analysis depends only upon direct measurements with instruments and at no stage upon the judgment of the analyst. The determinations made by an intelligent laboratory assistant are as reliable as those made by the spectroscopist who developed the method.

Articles printed on pages 59 to 88, inclusive, were presented at the Symposium on Recent Advances in Methods for the Determination of Traces.



## Field of Application

The foundation of this method for qualitative analysis was laid by Bunsen and Kirchhoff in 1860-1861 and for quantitative analysis by Hartley in 1882. However, the method had little practical application for many years because the procedures employed were not readily reproducible and the quantitative results were not sufficiently accurate. In recent years the field of application of this method has been considerably enlarged and its practical success ensured by the development of improved technique. The sensitivity, accuracy, and speed have been greatly increased by the use of spectral sources of excitation particularly adapted to the analyses of different types of materials and by the use of well-tested means of measuring the intensities of spectral lines.

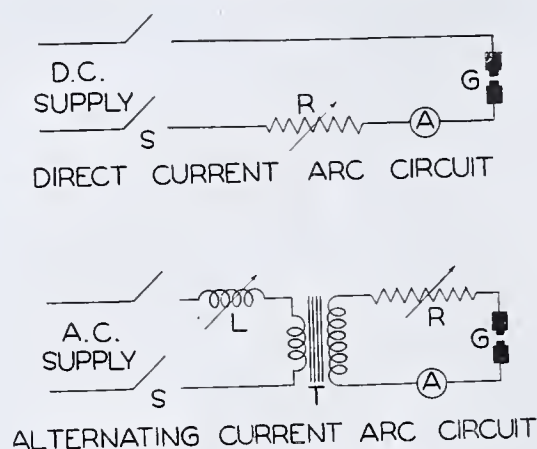


FIGURE 1. CIRCUIT DIAGRAMS  
Direct current arc and high-voltage alternating current arc sources

S. Line switch	R. Variable resistance
L. Variable inductance	A. Ammeter
T. Transformer	G. Analytical arc gap

The applications of the method now include the analyses of practically any solid, liquid, or powdered material containing metallic or metalloid constituents or impurities. Its advantages have led to its regular use for quantitative control analyses of several commercial products, including metals, alloys, and heavy and organic chemicals. In addition, it has proved valuable for quantitative trace analyses of biological, agricultural, and geochemical specimens.

## Experimental Technique

**EXCITATION OF SPECTRA.** The chief factor in the sensitivity of spectrographic analysis is the type of spectral excitation employed. The sensitivity, as well as the analytical accuracy, has been considerably increased by the use of spectral sources particularly adapted to the analyses of different materials. The following sources have been found to be appropriate for the analyses of the indicated types of materials for small amounts of impurities:

Inorganic chemical products: the high-voltage, alternating current arc

Metallurgical specimens: the direct current arc

Geochemical samples: the cathode layer of the direct current carbon arc

Organic chemical and biological materials: the direct current condensed spark and the high-voltage, alternating current arc

These classifications are not rigid, but indicate the most favorable sources as found in practice.

**Direct Current Arc.** The wiring diagrams of the direct current and of the high-voltage, alternating current arcs are shown in Figure 1.

The direct current arc is maintained between two electrodes of an electrically conducting, solid sample, or between

two graphite or metallic electrodes in a cavity of one of which a small amount of a powdered or liquid sample is placed. Arc currents of from 1 to 15 amperes are ordinarily used. The sensitivity of detection of impurities usually increases with the current on account of the higher temperature attained.

**Cathode Layer of Direct Current Carbon Arc (12).** In contrast with usual direct current arc practice, in this source the sample material is placed upon the cathode. This source utilizes the experimental fact that in a region 1 to 2 mm. from the cathode the intensities of the spectral lines of most metals are enhanced from 5- to 100-fold over their intensities in the positive column of the arc. This enhancement is produced by an increased concentration of metallic atoms in that region which is caused by the ionization of vaporized atoms in the arc gas, the migration of these ions to the cathode, and their neutralization there. This enhancement is most pronounced for small amounts (1 to 3 mg.) of sample and is decreased by adding to the sample a large amount of a substance of lower ionization potential than the test element. This source has proved particularly valuable for the analysis of nonconducting geochemical samples for minute traces of impurities (16).

**High-Voltage, Alternating Current Arc (5, 14).** Arc currents of from 1 to 6 amperes are ordinarily used at potentials of 1,100 or 2,200 volts. The arc may be maintained between solid electrodes of the sample or between two graphite or metallic electrodes upon each of which a drop of the test solution has been dried.

This source has been found to be extremely important for trace analyses of chemical materials. Its chief advantages include reproducibility of excitation conditions, high sensitivity, low background density, and small amount of sample required.

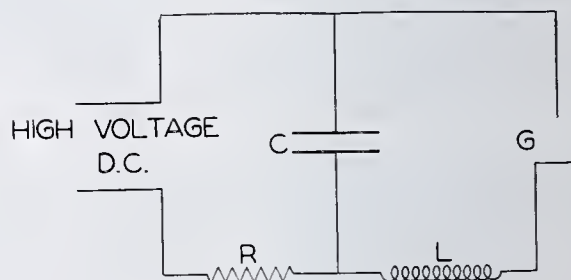


FIGURE 2. CIRCUIT DIAGRAM  
Direct current condensed spark source  
R. High resistance L. Inductance  
C. Capacitance G. Analytical spark gap

**Direct Current Condensed Spark (10).** While the high-voltage, alternating current condensed spark is advantageous for the analyses of metallic alloys for constituents in amounts greater than 0.1 per cent, the low-voltage, direct current condensed spark is suitable for trace analyses of biological materials. A wiring diagram of the latter spark circuit is shown in Figure 2. As used, the spark takes place between a plane metal electrode upon which the sample is spread and a pointed metal electrode.

The advantages of this source include high sensitivity concentration of the radiation in the arc spectrum, low background intensity, and no ashing and only minimum amount of chemical preparation of the small amount of sample required.

**Summary of Spectral Sources.** The direct current arc is suitable for the analysis of material in the solid, powdered or liquid state. While the alternating current arc and the direct current condensed spark may be used directly for the analysis of solid electrodes, they are best suited, with presen-



usage, for the analysis of solutions which have been evaporated on the electrodes.

The average absolute sensitivities, in terms of the amount of metallic element determinable on the electrode, of the sources described are:

Direct current arc	$10^{-5}$ to $10^{-4}$ mg.
Cathode layer of direct current carbon arc	$10^{-6}$ to $10^{-5}$ mg.
High-voltage, alternating current arc	$10^{-6}$ to $10^{-5}$ mg.
Direct current condensed spark	$10^{-6}$ to $10^{-4}$ mg.

PHOTOGRAPHIC PHOTOMETRY. The development of precise methods of spectral photometry in recent years has contributed more than any other factor to the marked improvement in analytical accuracy.

Early methods for determining the concentration of a test element in a specimen were based upon various modifications of the general procedure of estimating, by visual inspection, the abundance of the element by reference to a series of standard spectra in which this element was varied over a known range.

TABLE I. ANALYSIS OF CAUSTIC LIQUORS

Test Element	Range of Analysis, 25% NaOH Solution %	Sensitivity (Element on Electrodes) Mg.
Al	0.000053-0.0074	$2.5 \times 10^{-6}$
Ca	0.000039-0.0036	$2.0 \times 10^{-6}$
Mg	0.00003-0.022	$1.5 \times 10^{-6}$
Si	0.0005-0.05	$2.5 \times 10^{-4}$
Cr	0.00002-0.01	$1.0 \times 10^{-5}$
Cu	0.00001-0.005	$5.0 \times 10^{-6}$
Fe	0.00001-0.01	$5.0 \times 10^{-6}$
Mn	0.000002-0.00052	$1.0 \times 10^{-6}$
Ni	0.000075-0.01	$3.8 \times 10^{-5}$
Pb	0.00002-0.0034	$1.0 \times 10^{-5}$
Sr	0.00001-0.01	$5.0 \times 10^{-6}$

The analysis is now made, in best practice, by a photometric measurement of the true relative intensity of a line of the test element and of a line of a control element present in or introduced into the specimen in constant amount (7, 11). This relative intensity is a measure of the concentration of the test element. The actual relationship is experimentally determined for each element by measurements made upon the spectra of a series of specimens of known composition in which the test elements vary over the desired ranges. The graph of this relationship, illustrated in Figure 3, provides an analytical curve from which future analyses are made (15). Photometric technique is now sufficiently reliable to limit the error in the measurements of relative intensities to less than  $\pm 5$  per cent.

Representative Trace Analyses

The following representative analyses are briefly described in order to illustrate the diversity of the successful applications of quantitative spectrographic trace analyses and to give the technique found most suitable in each case. The ranges of abundance of the test elements, as given, are not necessarily the only ranges in which the analyses may be made, but are those of practical interest. The sensitivity of determination of each element corresponds to the lower limit of the range of analysis for that element.

HEAVY CHEMICALS. A representative application in the field of heavy chemicals is the analysis of caustic liquors, especially those supplied to the rayon industry, for the metallic impurities: iron, silicon, aluminum, lead, manganese, chromium, calcium, copper, nickel, strontium, and magnesium (3). The spectrographic method provides the only practical means of analysis for these impurities in their usual concentration ranges.

One drop of a 25 per cent sodium hydroxide solution is vaporated on each of two purified graphite electrodes and the spectrum of the dry salt residue is excited in an alternating current arc. Only about 12 mg. of dry sodium hydroxide

are used in the arc. The analysis is made from analytical curves, determined for each element by means of the relative intensity of a line of the test element and of a line of molybdenum, the internal standard introduced into each solution in constant amount. A typical analytical curve is shown in Figure 3.

The percentage ranges under analysis and the sensitivity are given in Table I. The absolute limit of detection is approximately  $1 \times 10^{-6}$  mg. of test element upon the electrodes.

This method is not only considerably faster but also more accurate than the corresponding chemical analysis. The average error amounts to no more than 5 to 10 per cent of the amount present.

TABLE II. ANALYSIS OF ORGANIC CHEMICALS

Test Element	Range of Analysis %	Sensitivity (Element on Electrodes) Mg.
Fe	0.0001-0.02	$6 \times 10^{-5}$
Cu	0.0001-0.02	$6 \times 10^{-5}$
Al	0.0001-0.01	$6 \times 10^{-5}$
Ca	0.0001-0.01	$6 \times 10^{-5}$
Mg	0.0001-0.01	$6 \times 10^{-5}$
Mn	0.0001-0.01	$6 \times 10^{-5}$
Pb	0.0001-0.01	$6 \times 10^{-5}$
Si	0.0001-0.01	$6 \times 10^{-5}$
Sn	0.0001-0.01	$6 \times 10^{-5}$
Sr	0.0001-0.01	$6 \times 10^{-5}$
Ni	0.0003-0.02	$1.8 \times 10^{-4}$
Zn	0.0005-0.01	$3 \times 10^{-4}$

ORGANIC CHEMICALS. Organic chemicals of various types, including plastics, are analyzed for the metallic impurities in the concentration ranges given in Table II (4).

The sample (0.40 gram) is prepared for analysis by digestion in mixtures of spectroscopically pure sulfuric, nitric, and perchloric acids, and to the resulting solution are added suitable internal standards and a sodium salt to serve as a spectroscopic buffer. The spectral source consists of an alternating current arc between two purified graphite electrodes upon each of which 0.03 ml. of the prepared solution

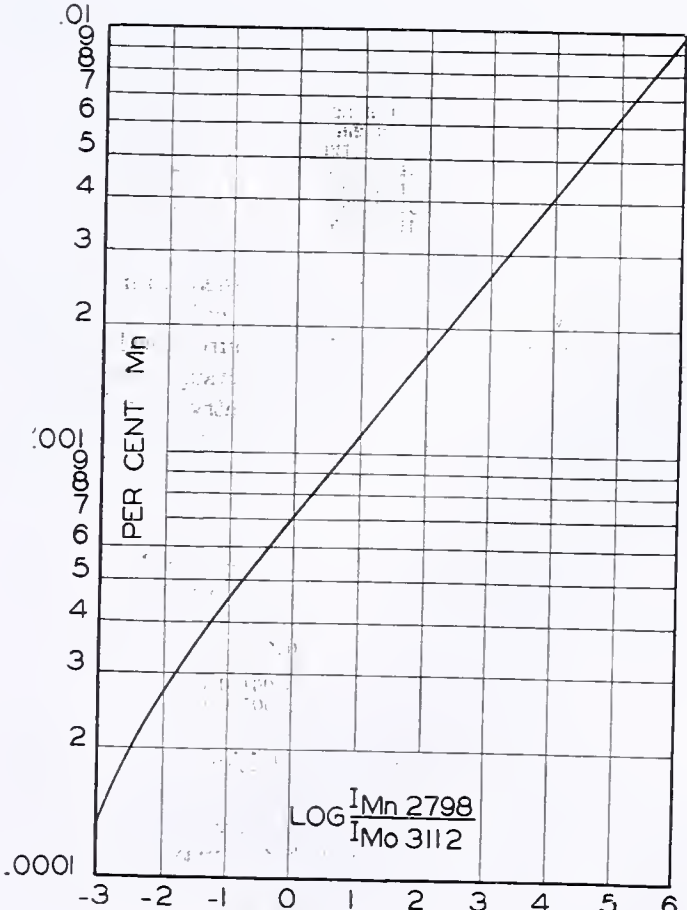


FIGURE 3. TYPICAL ANALYTICAL CURVE  
Analysis of caustic soda for manganese



has been dried. The photometric method is identical with that used for the analysis of caustic liquors.

Under the usual conditions of analysis of a batch of six samples, the time required for the determination of each test element is about 5 man-minutes. The average error, obtained by repeat analyses of the same specimen, amounts to approximately 10 per cent of the amount present.

TABLE III. ANALYSIS OF ZINC

Material	Test Element	Range of Analysis %	Sensitivity (Element on Electrode) Mg.
Pure zinc	Pb	0.0002-0.10	$1 \times 10^{-4}$
	Fe	0.0001-0.10	$5 \times 10^{-5}$
	Cd	0.00005-0.10	$2.5 \times 10^{-5}$
Zinc alloy die casting	Mg	0.004-0.25	$1.3 \times 10^{-3}$
	Ni	0.004-1.0	$1.3 \times 10^{-3}$
	Cu	0.0005-1.0	$1.7 \times 10^{-4}$
	Fe	0.0005-1.0	$1.7 \times 10^{-4}$
	Pb	0.0004-0.10	$1.3 \times 10^{-4}$
	Cd	0.00005-0.10	$1.7 \times 10^{-5}$
	Sn	0.002-0.05	$6.6 \times 10^{-4}$

**METALLURGICAL SPECIMENS. Zinc.** The compositions of pure zinc and of zinc alloy die castings are regularly checked spectrographically for the impurities given in Table III (2).

The spectra are obtained with a 15-ampere direct current arc between graphite electrodes. The positive electrode is treated with an acid solution of the test sample. The analysis is made by visual comparison of the spectrum of the test sample with the spectra, placed upon the same plate, of standard samples of known composition with a precision of  $\pm 10$  per cent of the amount present. This method will consistently detect an offgrade composition if the concentration of any test element is 20 per cent or more higher than the corresponding concentration in the standard.

**Lead.** The spectrographic method is employed to analyze high-grade pig lead for the impurities shown in Table IV (1). The technique used and the accuracy obtained are similar to those of the analysis of zinc.

TABLE IV. ANALYSIS OF LEAD

Test Element	Range of Analysis %	Sensitivity (Element on Electrode) Mg.
Cu	0.0001-0.32	$2 \times 10^{-5}$
Bi	0.001-0.256	$2 \times 10^{-4}$
Ag	0.0001-0.128	$2 \times 10^{-5}$
Ni	0.001-0.128	$2 \times 10^{-4}$
Sb	0.001-0.10	$2 \times 10^{-4}$
Sn	0.001-0.05	$2 \times 10^{-4}$
Cd	0.001-0.005	$2 \times 10^{-4}$

**Magnesium.** Control analyses of magnesium metal for the impurities given in Table V are made entirely by spectrographic methods (13). The spectral source used is a direct current arc between solid metal electrodes supported in water-cooled holders. The method of photometry is similar to that employed for the analysis of caustic liquors. The major constituent, magnesium, is used as the internal standard element.

TABLE V. ANALYSIS OF MAGNESIUM

Test Element	Range of Analysis %
Mn	0.001-0.05
Si	0.001-0.05
Fe	0.001-0.045
Ni	0.001-0.05

Under the usual experimental conditions the time required for a duplicate determination is 5 man-minutes. This is considerably more rapid than chemical analysis. In the range from 0.001 to 0.02 per cent, the maximum analytical error does not exceed  $\pm 0.002$  per cent of the test element. In the range above 0.02 per cent, the average error is about  $\pm 5$  per cent of the amount present.

**BIOLOGICAL MATERIALS. Body Fluids and Tissues.** An interesting recent development of the use of spectrographic methods has been their application to the studies of the human body and its functions.

Methods have been developed for the determination of sodium, potassium, calcium, and magnesium in urine, blood, and saliva (5, 18), and for lead in various body fluids and organic tissues (17). Since the concentration ranges of interest of sodium and potassium lie above 0.01 per cent, the analyses for these elements will not be considered.

The fluid or tissue is ashed and to the resulting acid solution are added suitable internal standard elements and a spectroscopic buffer. One drop of the solution is dried upon each of the graphite electrodes of an alternating current arc. The photometry is identical with that used for the analysis of caustic liquors. The range of analysis is shown in Table VI.

TABLE VI. ANALYSIS OF BODY FLUIDS AND TISSUES

Material	Test Element	Range of Analysis %	Sensitivity (Element on Electrode) Mg.
Urine, blood, saliva	Mg	0.0005-0.05	$2 \times 10^{-4}$
	Ca	0.002-0.10	$8 \times 10^{-4}$
Body fluids, tissues	Pb	0.00001-0.01	$2.8 \times 10^{-5}$
Cerebrospinal fluid	Pb	0.000001-0.002	$8 \times 10^{-7}$

This method possesses the advantages of rapidity, accuracy, and the requirement of only a small sample. Ten milliliters of urine suffice for determinations of magnesium and calcium, while 2 ml. of urine or a few milligrams of skin or tissue suffice for an analysis for lead. The average analytical error is approximately 5 per cent of the amount present.

A similar method developed for the analysis of body fluids, organic tissues, and foods for lead by the use of the direct current arc and of a less precise method of photometry yields approximately the same sensitivity but about twice the error of the technique described above (3).

A technique has also been reported for the analysis of cerebrospinal fluid for lead, in the concentration range shown in Table VI, using a direct current condensed spark spectral source (10). One milliliter of material, which is neither ashed nor previously chemically treated, is sufficient for several determinations. A unique analysis is made of each specimen by a comparison of the relative intensities of spectral lines of lead and of an internal standard element before and after the addition to the sample of a known amount of lead. The analytical error is less than 15 per cent and two samples may be analyzed in 3 hours for lead in a concentration range in which chemical methods are not reliable.

TABLE VII. ANALYSIS OF PLANT ASH

Test Element	Range of Analysis (In Solution on Electrode) %	Sensitivity (Element on Electrode) Mg.
Ca	0.0001-0.50	$1 \times 10^{-4}$
Fe	0.00005-0.20	$5 \times 10^{-5}$
Mg	0.0001-0.50	$1 \times 10^{-4}$
Mn	0.0001-0.50	$1 \times 10^{-4}$
P	0.001-1.0	$1 \times 10^{-3}$

**Plant Tissue.** Spectrographic analysis permits the determination of the distribution of elements, known to be necessary for proper growth and development, throughout a single plant and to some extent the following of this distribution throughout the life history of the plant.

A method has been developed, by the use of essentially the same technique as that used for the analysis of cerebrospinal fluid, which permits the analysis of as little as 200 mg. of plant tissue for boron in the range from 0.0001 to 0.001 per cent (9);  $1 \times 10^{-4}$  mg. of boron on the electrode is determinable. The analytical error rarely exceeds  $\pm 10$  per cent and one hour is required per determination.



A procedure which is applicable to samples of even less than 10 mg. has also been worked out for the analysis of plant ash for the minor impurities shown in Table VII (8).

A 50-mg. sample (if available) of ash is treated with hydrochloric acid and diluted to 10 ml. with a sodium chloride-ammonium chloride buffer solution. The spectrum of 0.1 ml. of this solution is excited in a 15-ampere, direct current graphite arc. The analysis is made upon the basis of a microphotometric comparison of the blackenings of the lines of the test elements in the specimen with those in standard solutions. The analytical error is ordinarily less than  $\pm 10$  per cent of the amount present.

TABLE VIII. ANALYSIS OF GEOCHEMICAL MATERIALS

Test Element	Lowest Concentration Determined %	Sensitivity (Element on Electrode) Mg.
Li	0.000047	$1.4 \times 10^{-6}$
Be	0.00036	$1.1 \times 10^{-5}$
B	0.00016	$4.7 \times 10^{-6}$
La	0.00085	$2.6 \times 10^{-5}$
Co	0.0037	$1.1 \times 10^{-4}$
Ni	0.0005	$1.5 \times 10^{-5}$

**GEOCHEMICAL SAMPLES.** Investigation of the abundance and geochemical distribution of the chemical elements required the development and use of sensitive physical methods of quantitative analysis of rocks, minerals, glasses, slags, ashes, clays, and soils which would determine most elements down to concentrations of 0.001 per cent or less. Spectrographic methods that utilize the excitation of spectra in the cathode layer of the direct current carbon arc have successfully fulfilled these requirements (16). Representative examples of such analyses are given in Table VIII.

In analysis for lithium in mineralogical specimens a few milligrams of the sample are ground and mixed with strontium oxide, the internal standard, and approximately 3 mg. of the mixture are packed into a cavity in the negative electrode of a 10-ampere carbon arc. The photometric method is similar to that used for the analysis of caustic liquors. A single spectrum gives a possible error of  $\pm 25$  per cent, while the average of four spectra limits the error to less than  $\pm 5$  per cent. One operator can make 64 analyses per day.

This technique yields a rapid, precise, highly sensitive, quantitative analysis of a few milligrams of chemically untreated mineralogical sample.

### Acknowledgment

The writer is indebted to T. M. Hess for many helpful discussions during the preparation of this manuscript.

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## Fluorescent Analysis of Inorganic Materials

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**FLUORESCENT** analysis has been given added impetus in recent years by the contributions of a great many workers. The reviews prepared by Radley and Grant (19) in England, and Haitinger (13) and Danckwortt (5) on the continent have assisted greatly in focusing attention upon this subject. The recent interest of textbook editors in fluorescent analysis is attested to by the fact that Feigl (8) in the 1938 edition of his text on Spot Test Reactions has included a section giving a general discussion of the technique of fluorescent analysis; and under the specific test for the elements he designates fluorescent methods in at least a half dozen cases. In some instances the tests are entirely new, while in others the sensitivity is greatly increased by examination in ultraviolet light.

It is admitted that as an inorganic laboratory tool fluorescence is still in its early stage of development. The progress has been handicapped by inconvenient light sources and apparently limited applications.

It is the object of this paper to outline the progress in this field, with the hope that it may stimulate an interest which will lead to a broader use of this interesting phenomenon in inorganic work. The general applications of fluorescent analysis in organic chemistry, in criminological work, in biology, medicine, and pharmacy, and in other branches of science will not be included. However, it is sometimes difficult to limit a field of this sort—for example, the organic chemist may use an inorganic substance in identifying his compounds; or as in fluorescent chromatographic analysis, an inorganic absorbent is used to separate the organic materials.

The term "fluorescence" is a broad one, embracing secondary rays of many different wave lengths, and is used chiefly to designate the visible light emitted when a substance is brought under the influence of an invisible exciting source. Many of the secondary rays produced may be too short or too long for direct identification by the eye, and a wave motion between 4,000 and 8,000 Å. may cause the emission of another visible



ray; but present analytical applications of these extremes are so limited that they will not be considered.

### Sources of the Exciting Ray

Fluorescence may be excited in many different ways: by cathode rays, radium rays, x-rays, etc. A recent article (9) indicates that cathode rays were used in studying the fluorescence of eighty specimens of calcite. It is, however, the near ultraviolet that is the most generally applicable, and the discussion here will be confined to the methods of producing the rays essentially between 3,000 and 4,000 Å. In any case the excitation source should always be carefully described, as some of the contradictions appearing in the literature may be due to the use of varying intensities of ultraviolet rays. In general, the strongest source available should be used so that no obscure phenomenon may be overlooked.

The spark or arc discharge between metallic electrodes such as iron, nickel, cobalt, aluminum, tungsten, magnesium, and cadmium, and the impregnated electrodes where the core contains aluminum, tungsten, etc., provides an intense source and one rich in the shorter wave lengths. The arcs have been developed to a point where they are slow-burning and may be used for some time without attention. The iron arc is often recommended where observations are to be made under a microscope, since the ultraviolet must travel by way of a lens and prism or mirror before it is used, and an original intense source is necessary. Of the metals mentioned iron, tungsten, and molybdenum give the greatest number of lines between 2,000 and 4,000 Å. Practically all the metallic and impregnated carbon electrodes give resulting spectra with greater number of lines and with greater intensity than the mercury arc.

The disadvantages of the electrode arc lamps are well known, but with proper equipment such as that developed by Reichert, the electrodes can be handled in a satisfactory manner.

For this so-called Haitinger-Reichert lamp, Haitinger has developed an iron electrode, consisting of an iron tube packed with an iron and carbon core, which burns smoothly and does not form the iron oxide film as does the ordinary rod electrode. The current consumption of this lamp is only 4 amperes on direct current or 8 amperes on alternating current, which means that the metal electrodes will burn away very slowly. The lamp will burn for hours at a time without adjustment of the electrodes.

Another type of iron arc lamp, a vacuum arc, has been advertised recently by Kipp and Zonnen. This was developed at the suggestion of Professor Zeeman of Amsterdam and is easily evacuated to a pressure of 4 cm. of mercury with an ordinary filter pump. The arc burns slowly in a constant way.

Next to the arc lamps the quartz mercury vapor lamp is most favored.

The analytical model manufactured by the Hanovia Company is widely used. This lamp is designed with a cylindrical hood and special reflectors which greatly increase the efficiency of the quartz mercury arc source. The front of the lamp is fitted with an easily removable filter which removes most of the visible radiations. The intensity of this lamp is reported to decrease slowly during the first 400 hours of operation and then remain practically constant for several thousand hours of use. The short wave lengths emerging through the quartz cause a considerable quantity of ozone to be formed, and since this gas is poisonous even in small quantities some means should be provided for its removal. An ordinary ventilating fan is satisfactory for this purpose.

There are many models of mercury vapor lamps on the market and most of these will give some degree of satisfaction. Another type of mercury vapor lamp is known as the high-pressure mercury arc lamp, such as the H4 of the G.E. Vapor Lamp Company. One important asset of these lamps is their simple operation and low original cost. With a small ballast transformer they operate on any 110-volt line. Their greatest intensity in the ultraviolet is, in general, around 3,660 Å. which is ample for most routine laboratory work. The outside envelope may be entirely

removed or a hole bored in it to obtain radiations below 3,500 Å. If the lamp is enclosed so that the visible rays are removed by a filter it must be cooled by air circulation so as to approximate conditions in an open room. Commercial units of this sort are available. Some of the mercury vapor lamps are made with dark glass so that they may be applied directly in fluorescent work. These are designed especially for demonstration purposes and are not recommended for general laboratory practice.

Another source of the near ultraviolet which will produce fluorescence is the well-known argon bulb. The intensity of this is so low that its application is limited. For example, some tests which are good to 1 part in 10,000,000 under the quartz mercury vapor lamp will detect only 1 part in 100,000 with the argon bulbs. A battery of these bulbs has been applied in the quantitative determination of riboflavin (24). Here riboflavin is compared to a fluorescein standard and the authors claim excellent results.

### Filters

In considering a source of ultraviolet rays the filter used becomes an important factor and its type and thickness should always be designated. By reference to any manufacturer's catalog of glass filters, such as Corning or Jena, one may determine the type desired for a particular job. Where intensity is a factor the thickness of the glass is also significant—for example, an 8-mm. nickel oxide glass decreases the intensity of the iron arc too greatly for some microscopic examinations, and 3 mm. permits the passage of too much visible light. A 5-mm. filter serves as a compromise. In addition to glass filters, gelatin, Cellophane, and colored solutions such as those of copper and nickel salts, are employed with much satisfaction. A list of solutions to isolate the important lines between 2,480 and 5,790 Å. has been published (2, 7, 22).

The intensity of the ultraviolet light used may be determined by chemical reactions, spectrographic methods, or photonic cells. The Westinghouse Company has designed a photoelectric apparatus for this particular purpose. It is believed, however, that if the type of lamp, the filter, and distance of operation are specified, it is not necessary to report the actual intensity of the ultraviolet light.

### Condition of Sample

The sample to be observed may be in the solid, liquid, or gaseous condition. If the substance is a solid, the size of the particles becomes important. Too large or too small a particle may not fluoresce at all, or may have a different appearance from one of intermediate size. Borax, phosphate, or fluoride beads serve well for examining many inorganic substances. In the liquid examinations the solvent should be nonfluorescent if possible. A solvent fluorescing in the green may completely mask a substance giving a red fluorescence. The concentration, temperature, and acidity of the solution all have some effect upon the luminescence. In the case of the concentration the result is fairly obvious, the nature of the color does not change, but the intensity fades with increasing dilution. In a recent article on the fluorescence of the rare earths (21), the authors indicate that a wide variety of temperatures was used in their study. The acidity of the solution is of some moment. Some materials not fluorescing at all in a neutral solution may do so in an acid or alkaline medium. In the morin test for aluminum, scandium, gallium, and indium Beck (1) has shown that the fluorescence is strongest in a little mineral acid. Sodium acetate and sodium fluoride weaken the fluorescence in this case. Materials responsive to oxidizing and reducing agents are, of course, affected if these are present—for example, it is only the lower valence of mercury, copper, and tellurium that fluoresces.



Quartz containers are the best for transmitting the ultraviolet. However, if an ordinary filter is used on the lamp source, one may just as well use glass containers, since the lower limit of transmission is about 3,000 Å. in both cases. The fluorescence of the container should always be tested before attempting to use it in analysis. Ordinary white spot plates will fluoresce in the purple, and black ones in the green. Glass spot plates can be used satisfactorily. The fluorescence of a material may be observed sometimes much better in a test tube than on a spot plate. This is true in the case of the Blue Black R test for aluminum. The test is visible only with transmitted light. Spot test paper, either black or white, is satisfactory in many cases. Here again the fluorescent property of the paper and also the reagent must be tested. Some reagents, especially the dyes, will not fluoresce in water solution but show a brilliant fluorescence when placed on spot test paper. Minute quantities of solutions may be tested by placing a drop between quartz microscope slides and observing this in both reflected and transmitted light either with or without the microscope.

Reichert (20) has designed an excellent apparatus for microscopic observations. In this arrangement the light passes through a collecting lens system, a glass filter, and a copper sulfate solution filter. The latter removes all of the red rays and this prevents undue heating of the object. Filters are used on the eyepieces to remove the wave motions below 4,000 Å. which are likely to injure the eye. The microscope may be provided with a spectroscopic or spectrographic attachment, so that the fluorescent light may be analyzed. If the solution is allowed to crystallize, the fluorescence of the crystal is often much more intense than that of the solution. Attachments for fluorescent work may be placed on almost any microscope. Both incident and transmitted ultraviolet arrangements are used.

For examination in a macro way the containers may be placed directly under or in front of the lamp. The arrangement used by Haitinger and Reich (15) is satisfactory. Here the ultraviolet light enters the top of the tube and the depth to which it penetrates depends somewhat on the concentration.

The fluorescent color should always be described in terms of Angstrom units. It is rather indefinite to say that a material gives a green fluorescence, since there is such a wide variety of greens and it is difficult to describe a particular shade. The use of a spectroscope, spectrograph, colorimeter, photometer, or Lovibond tintometer will more accurately convey the idea of the region of the spectra involved.

### Quantitative Methods

Quantitative methods using fluorescence have been applied successfully in organic analysis, but little has been done with inorganic materials. We have already mentioned the simple method used in the determination of riboflavin. Cohen (4) in Holland has applied the selenium photronic cell to the measurement of fluorescence of lactoflavins, and this method might be applied to inorganic solutions. Results were satisfactory to  $2 \times 10^{-5}$  gram per ml. and were accurate within 3 per cent. The curve which Cohen obtains from his data is typical for fluorescent solutions. At the lower concentrations there is a straight-line relationship between intensity and concentration, but at higher concentrations the solution reaches its saturation point as far as fluorescence is concerned. As far back as 1925 Lutz (16) reported a quantitative fluorescent micromethod for zinc, where he used urobilin as the reagent and compared the intensity with Nessler tubes. The method will detect 0.01 to 0.5 mg. of zinc in 50 ml. within a 10 per cent error.

The Pulfrich gradation photometer gives a rapid and satisfactory method of determining concentration from the intensity of the fluorescence. In the recommended apparatus both liquid and solid filters are used, and a special glass is inserted to

remove any ultraviolet before it reaches the eye of the operator. Cells of any size may be used and this may be classed as a micro-method. The high light-transmitting power of the Pulfrich is especially advantageous for measuring the feeble intensities of fluorescent light. The Pulfrich is also adaptable to the measurement of the fluorescence of solids. In this case a piece of uranium glass or other solid may be used as a standard, and by interposing correct filters the intensity of any fluorescing color may be measured.

Matheson and Noyes (17) use a photoelectric cell and a DuBridge circuit with an F. P. 54 tube for measuring the fluorescence of acetone. Byler (3) uses the MacBeth illuminometer manufactured by the Leeds & Northrup Company to measure the intensity of the fluorescence of calcium phosphates. With this instrument he measures intensities as low as about 0.6 per cent of grade A zinc sulfide and differences as low as 0.08 per cent.

Spectrographic and photographic methods may be used in quantitative measurements, but these seem to be more or less troublesome.

Confined spot tests, as developed by Yagoda (26) and capillary adsorption on filter paper should find some semi-quantitative application for inorganic fluorescent analysis.

### Applications

The inorganic materials that fluoresce are rather well classified by Radley and Grant (19). Fluorescent methods are not generally applied in mineral identifications. Of the many known minerals only about forty are fluorescent and the mineralogist knows these so well that special methods are not necessary. However, the detection of traces of elements in minerals may sometimes depend on fluorescent methods. Haberlandt and others (12) claim that the fluorescence of fluorite is due to divalent europium, because europium chloride gives the same bands in both the red and blue as does fluorite. The blue band is sensitive to  $10^{-6}$  gamma. A fluorescent study of sapphires and rubies (23) indicates that they both contain the same element, probably chromium.

Uranium is most easily detected in traces by the strong fluorescence of solid uranyl salts; 0.001 gamma in a concentration of one in a million is evident. This finds application also in the zinc uranyl acetate test for sodium, which is made much more sensitive if the material is examined in ultraviolet light. In ordinary light the limit of the test is 12.5 gamma at a concentration of 1 in 4,000, in ultraviolet 2.5 gamma at 1 in 20,000. The fluorescence of uranyl salts is decreased by the presence of strong oxidizing or reducing ions. The inhibition of fluorescence by added agents seems unpredictable. Addition of 0.5 part per million of nickel to zinc sulfide prevents its fluorescence. Ozone has been determined by its decreasing the brilliance of fluorescein. Activators operate in an opposite manner. Copper and manganese seem to increase the fluorescence of zinc sulfide. It is believed that traces of activators or inhibitors can be detected by their effect upon fluorescent material sufficiently for a qualitative identification.

The effect of pH changes on fluorescence is so striking that this may be used to determine the end point of a titration. Dérivé (6) gives a table of thirty-seven organic substances with their pH limits and the effect of oxidizing and reducing agents. There are many interesting applications of indicators of this type. Gotô (10) employs alpha-naphtholflavone for iodometry. The blue fluorescence of this substance disappears in the presence of free iodine or bromine and reappears when these halogens are removed. This can be used in the titration of iodine by sodium thiosulfate and in the titration of arsenious acid by potassium bromate. Ohac (18) titrates  $Al^{+++}$  with sodium fluoride, using morin as a fluorescent indicator. In these titrations a small vial of quinine sulfate may be floated in the buret to read the meniscus.



In most inorganic tests using organic materials the pH must be somewhat controlled. The molybdenum test using tincture of cochineal which is sensitive to 0.02 gamma of molybdenum oxide must be carried out at a pH between 5.7 and 6.2.

It is hoped that fluorescence will add to the specific test for the elements. Such a case is illustrated in the Pontachrome Blue Black R (25) test for aluminum, which is sensitive to 0.2 gamma of aluminum-ion concentration and to a dilution of one part in ten million. It serves to distinguish aluminum from all other elements investigated, and is the first direct chemical test to differentiate it from beryllium. The morin fluorescent test for aluminum is more sensitive and will detect 0.05 gamma at 1 part in 10,000,000 but is given also by beryllium, indium, gallium, and the rare earths.

In addition to the examples given, fluorescent tests, all of microapplication, have been worked out for beryllium, zinc, arsenic, tin, bismuth, manganese, cadmium, columbium,  $H_3BO_3$ , and  $H_2SO_3$ . A detailed description of these is given by Haitinger (14). Gotô (11) lists fluorescent methods for about twenty-one elements. This indicates fair progress in the development of fluorescent determinations. Fluorescence is in position at present to claim precedent over standard procedures in only a few cases. Indications are, however, that many more applications will be forthcoming and fluorescence will take its place in general inorganic analysis.

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# Isolation and Determination of Traces of Metals

## The Dithizone System

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COMPLEX organic compounds have become increasingly popular for qualitative and quantitative determination of metals. Such compounds, sometimes highly colored and often soluble in organic solvents, under definite conditions form complexes with certain metals that are likewise often highly colored and soluble in solvents immiscible with water. It is the favorable extraction coefficient, the intense color, or both, that has greatly interested analysts. Many convenient analytical separations have been based on such extractions even when the complexes produced were colorless, and when they possessed a high degree of color, colorimetric methods, often of surprising accuracy, were developed soon after the discovery of the complex. These newer chemical methods have been used to determine smaller and smaller quantities of metals, until what was considered a microquantity a few years ago is now lightly spoken of as almost of macro proportions. It was even necessary to use new units of measurement. One speaks now of micrograms or gammas to divide the milligram, the microchemical unit of former days.

Diphenylthiocarbazone (phenylazothionformic acid phenylhydrazide), usually abbreviated to "dithizone," is a highly colored organic compound that produces brilliant yellow, red, or violet colored complexes with a dozen or more metals. It is exceedingly useful in extracting a whole group and, under the proper conditions, separating subgroups and determining the individuals thereof. Dithizone is

therefore not a specific reagent, but under specific conditions it has become an excellent example of recent trends in chemical analysis and a new tool that has enabled chemists interested in the isolation and determination of traces of metals to extract and determine rapidly near-spectroscopic as well as milligram quantities of certain metals with an accuracy greater than that found in spectroscopic determinations, and without highly expensive apparatus or extensive experience. Herein lies its great value. This is not an implication that dithizone methods will ever supplant the spectroscope. The most useful range of dithizone methods is from 1 to 200 micrograms, and the errors vary from less than 1 per cent to 5 per cent, depending somewhat on the amounts to be determined. Therefore it may be said that dithizone methods begin about where spectroscopic methods usually leave off, and the two should be able to exist side by side. The dithizone system of analysis, however, does give the chemist in the ordinarily equipped chemical laboratory an excellent chance to compete in a complicated and highly technical microchemical problem at the added expense only of preparing slightly larger samples and taking extra precautions in the purification of reagents and prevention of contamination. Perhaps the same might be said about other purely chemical analytical systems of like sensitivity, but the dithizone system with its brilliant display of colors has certainly captured the imagination of a great many analysts, and has become the principal contender in this special field.



Hellmut Fischer, a metallurgist, is the father of the dithizone system of analysis. He and his co-workers have published numerous papers on the analytical properties of dithizone and its use in microanalysis, and a detailed review of dithizone literature up to 1938 from Fischer's pen may be found in *Angewandte Chemie* (9). In the United States the biochemists, pharmacologists, toxicologists, and food chemists have exhibited the greatest interest in dithizone, with the determination of lead as the focal point. This paper was written in an attempt to stimulate interest among other American chemists, especially the physical chemists, in this analytical field, and to promote the determinations of other "dithizone metals" besides lead. Attention will therefore be directed towards principles, and certain gaps in our present information will be emphasized with the hope that greater progress will be made. Perhaps a few speculations concerning future developments may also be of interest to this audience.

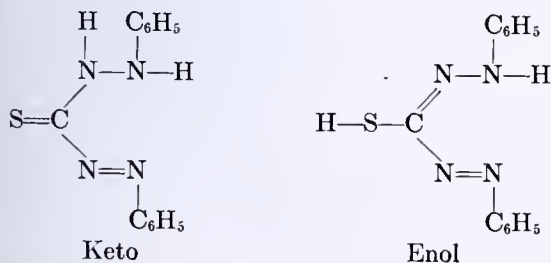
Analytical methods are divided into three parts—preparation of sample, isolation of the element sought, and its final determination. This paper is, therefore, divided in a corresponding manner.

### Sample Preparation

A discussion of sample preparation, especially in the case of biological material, is important, but for the purpose of this paper may be brief. Inorganic substances are usually dissolved in acids without much difficulty. Organic matter is destroyed by either wet or dry ashing where this is necessary. The dithizone system of analysis, being based on an extraction process, does not always require destruction of organic matter—for example, over 100,000 lead determinations have been made in the United States in the last year, on sprayed apples and maple sirup, wholly or partly by dithizone methods, without destruction of organic matter. In fact, a vigorous partial oxidation of organic matter with nitric acid, filtration, and aliquoting is often all that is necessary for sample preparation prior to a lead assay. The nitric acid brings insoluble lead compounds into solution, and breaks up or destroys colloids that cause emulsion formation or other difficulties in subsequent extractions of the metals with dithizone in organic solvents. Of course such treatment is not practical in all cases, and where it is not, some system of wet or dry ashing must be employed.

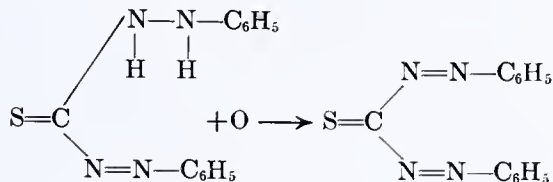
### Separations

Assuming that the sample has been properly prepared, the next step is the isolation of the metal desired, from aqueous solutions often containing interfering metals, as well as acids, salts, and sometimes organic matter. Since dithizone lacks specificity, separations are highly important and require careful consideration. Certain properties of dithizone and its complexes that influence separations are therefore discussed here.



Diphenylthiocarbazone exists, according to Fischer (8), in keto or enol form, the former being the more important analytically. It is very insoluble in water but soluble in ammonia and in many organic solvents, carbon tetrachlo-

ride or chloroform being the most convenient and practical ones. Fischer (9) believes that it is oxidized by mild oxidizing agents to the yellow, non-complex-forming, chloroform-soluble but water- and alkali-insoluble, diphenylthiocarbazone which may again be reduced to dithizone by reducing agents like hydroxylamine hydrochloride, or sulfites. American experience indicates that the two reducing agents mentioned are useful in preventing oxidation of dithizone. Stronger oxidation may attack the sulfur or break the compound at other places, with irreparable damage. A solution of pure dithizone in chloroform or carbon tetrachloride is stable if protected from direct sunlight and kept cool. Clifford (3) finds that overlaying a stock solution of dithizone in carbon tetrachloride with a 0.1 molar solution of sulfur dioxide preserves it unchanged for months if stored in the dark at ice-box temperatures.



Dithizone in solution has a tremendous tinctorial power and appears red or green, according to the concentration or the depth of the column through which it is viewed. It forms yellow, orange, red, or violet complexes with a dozen or more metals, almost all readily soluble in chloroform but less so in carbon tetrachloride. The "dithizonates" are simultaneously formed and extracted in most instances (platinum, palladium, and gold form colored flocks in carbon tetrachloride) by shaking aqueous solutions of the metals, at the proper hydrogen-ion concentration, with chloroform or carbon tetrachloride solutions of dithizone. The green color of excess dithizone in chloroform modifies the color of the extracted dithizonates with the production of beautiful so-called mixed colors ranging from green through blue, purple, and crimson to red in the case of the red dithizonates, according to the relative quantities of metal and excess dithizone. Mixed colors are not produced from alkaline aqueous solutions with carbon tetrachloride solutions of dithizone because dithizone is less soluble in that solvent, and the excess will largely dissolve in the aqueous phase.

Because both dithizone and the dithizonates are very soluble in chloroform and very insoluble in water, there is a most favorable partition coefficient if the hydrogen-ion concentration has been properly adjusted. Since the extracting solvent is heavier than water, repeated extraction can be made in separatory funnels without transfer of the solute. Minute as well as comparatively large microquantities of metals can therefore be extracted from even large volumes of aqueous solution by a process of "extractive enrichment," to use Fischer's expression (?). It is a matter of controlling the comparative volumes of the two phases and especially the concentration of the dithizone in the chloroform phase and the pH of the aqueous phase.

The various metals of the dithizone group react at different optimum hydrogen-ion concentrations of the aqueous phase. Therefore the pH governs the order in which the metals are extracted. Generally the more "noble" a metal is, the lower is its pH for optimal extraction. The metals, gold, platinum, palladium, silver, mercury, stannous tin, copper, bismuth, zinc, cobalt, nickel, lead, thallium, and cadmium react with dithizone in immiscible solvents more or less consecutively as the reaction of the aqueous solution is progressively changed from strong acid through weak acid, neutral, ammoniacal, and alkaline conditions up to 5 per cent of sodium hydroxide, but there are numerous coextractions.



Extractions of metals may be made at unfavorable pH with decreased efficiency, which may be in part overcome by paying special attention to the restriction of the volume of aqueous solution, increasing the volume and especially the concentration of the dithizone solution, and by vigorous agitation to bring the reactants into equilibrium. The separation of the different dithizone metals at any given pH is also modified by the relative quantities of the metals. The extraction of lead at pH 4, for example, is unfavorable, while that of mercury and copper is favorable. The mercury will tend to extract first and then will come the copper; but if the quantity of lead is large as compared with the other two, it may contaminate them to a certain extent.

If the effects of concentration of metals and of dithizone and hydrogen-ion concentration on the percentage of metal or metals extracted could be expressed in the form of equilibrium curves, there would be immediate use for them. Unfortunately, this has not yet been done, chemists generally being more interested in other phases of dithizone investigations. Were there equilibrium curves for the principal dithizone metals, one could see at a glance what metals would be coextracted under any given conditions and could, perhaps, even calculate their ratios or amounts. Naturally this would simplify separation problems. The Willoughby (28) separation of bismuth and lead at pH 2 is effective and illustrates what can be done by empirical methods. Were exact equilibrium curves available, they should show clearly the reason for this effectiveness, and the maximum departure from pH 2.0 permissible, to improve the ease of the extraction of bismuth without consequent loss of lead. Control of hydrogen-ion concentration is therefore the sieve that makes the first approximate separation of the dithizone metals.

The various dithizonates, when once formed and dissolved in the solvents under optimum conditions, vary in their stability toward acids. Lead, with an optimum extraction at pH 9.5, can be easily retransferred to the aqueous phase by shaking the chloroform solution of lead dithizonate with dilute acid. The alternate solution of lead in chloroform and acid phases can be repeated as often as wanted, and such alternate extraction may be utilized in the separation of lead from interferences of either metallic or nonmetallic nature. Zinc may be retransferred to the aqueous phase in a like manner, but it usually requires a little stronger acid or more shaking. Certain other dithizonates are comparatively stable towards dilute acids when once dissolved in chloroform and re-enter the acid phase with varying degrees of reluctance. Silver, mercury, and cobalt require rather strong acid to force them into the aqueous phase, while copper and nickel are more amenable to its action. A further study of the equilibria involved herein should pay dividends.

The metals also differ from one another in the stability of their dithizonates towards alkali. Lead dithizonate in chloroform solution becomes unstable towards aqueous alkali solutions at pH 11 or above and the lead begins to return to the aqueous phase where it may partly precipitate as the hydroxide. Bismuth and tin dithizonates will decompose, and the metals will return to the aqueous phase at a pH of 9 to 10. The critical pH governing the stability of zinc dithizonate is probably near 10.0, that of thallium near 11.0, and cadmium 12.0 or above. Bismuth and tin which are extracted with lead by dithizone have been separated from that metal by washing the dithizonates with diluted ammoniacal solutions at a probable pH value of about 10. The nature of the solvent also has an influence on the action of aqueous alkalis on dithizone and the dithizonates. Lead dithizonate in chloroform is more stable towards alkaline solutions than in carbon tetrachloride, the reversion point being approximately at pH 11.0 as contrasted to about pH 10.0 (20). Hellmut Fischer and associates, and other writers, have based determinations of

metals on washing the excess dithizone from carbon tetrachloride or chloroform solutions of dithizonates with weak ammonia solutions of 0.01 to 0.04 normality or mixtures of ammonia, cyanides, and sometimes ammonium chloride. It is admitted that the use of washing solutions that are too alkaline may result in metal losses due to the decomposition of some of the dithizonates, but the equilibria that govern the reversion of dithizonates by aqueous alkaline or acid solutions have been studied just as inadequately and empirically as those that produced them. Progress, therefore, seems to demand that the underlying principles be examined carefully, preferably by physico-chemical methods.

Before planning extensive equilibrium experiments the present state of our knowledge should be appraised. The solubility of the dithizonates in organic solvents depends upon a number of simultaneous equilibria, depending on concentration of metals and dithizone, variation in hydrogen-ion concentration of and presence of complex-forming salts in the aqueous phase, and partition coefficients of dithizone and dithizonates between solvent and aqueous phases. Such a complex system of simultaneous equilibria cannot be expressed in simple equations or curves. Nevertheless, the necessary basic ideas may be formed and much useful information may be gained by reducing the problem to the simplest terms. A beginning has been made with lead (6) by determining the percentage of lead extracted from a definite volume of aqueous solution of definite metal salt concentration by a definite excess of dithizone in chloroform over a useful hydrogen-ion concentration range. Such a system can be expressed by two coordinate curves. Increase or decrease of the metal or dithizone concentration would produce a family of curves by shifts towards the left or right, respectively.

Carbon tetrachloride as solvent would probably shift the curves about one pH unit to the left. Figure 1 shows a rough approximation of our present fragmentary knowledge. No pretense of accuracy is made in the drawing of these curves, since the basis for most of them is their analogy to lead and some bits of information picked here and there from the literature. These double sigmoid curves explain in a fashion many of the empirical facts found up to the present time in the development of dithizone methods of metal analysis. The writer hesitates to express an opinion on the ultimate shape of these curves when all the factors entering into the equilibrium are accounted for. Anyway, a consideration of the present curves gives useful information and furnishes a basis for an estimate of what the future may have in store. The curves of the metals shown in Figure 1 are based on the keto combination with dithizone. Silver and mercury are extracted from fairly acid solutions and therefore their curves are not expected to pass through the origin. In alkaline solutions beyond approximately pH 11.0, silver, mercury, and copper tend to produce the enol modifications, but since the conditions for this transition with respect to pH are not well known, only the acid extraction is symbolized. Thallium and cadmium dithizonates are stable in fairly alkaline solutions, but how much of an increase in alkalinity would be required to make them exhibit downward decomposition curves similar to other metals is unknown.

The significant part of these curves is the indication of an optimum pH of extraction and that different metals react best at often very different pH levels. Separations by pH control are based on these facts. But it is apparent that clean-cut separations of metals can be made only if the upper and lower parts of their curves (the future successors to the curves in Figure 1 are meant) do not overlap at the pH chosen for the extraction. When there is an overlapping indicating the probability of a small coextraction of an inter-



fering metal, such interference may possibly be reduced to negligible proportions by a number of alternate transfers between aqueous and immiscible solvents. Such a procedure resembles the double precipitation of macroquantitative analysis. The other alternative would be the extraction of the desired metal at a pH not optimum but where there is no overlapping. In any event, it does not need much imagination to realize that if we could replace this crude sketch with

Recently, organic competitive complexes have found a place in the complex fixation of dithizone interferences. Ritchie, as associate referee for the Association of Official Agricultural Chemists, and his associates (22) recommend diethyldithiocarbamate, the copper reagent, for interference fixation in the determination of zinc. They first extract all possible interfering metals as carbamates and dithizonates with carbon tetrachloride from aqueous solutions too acid for

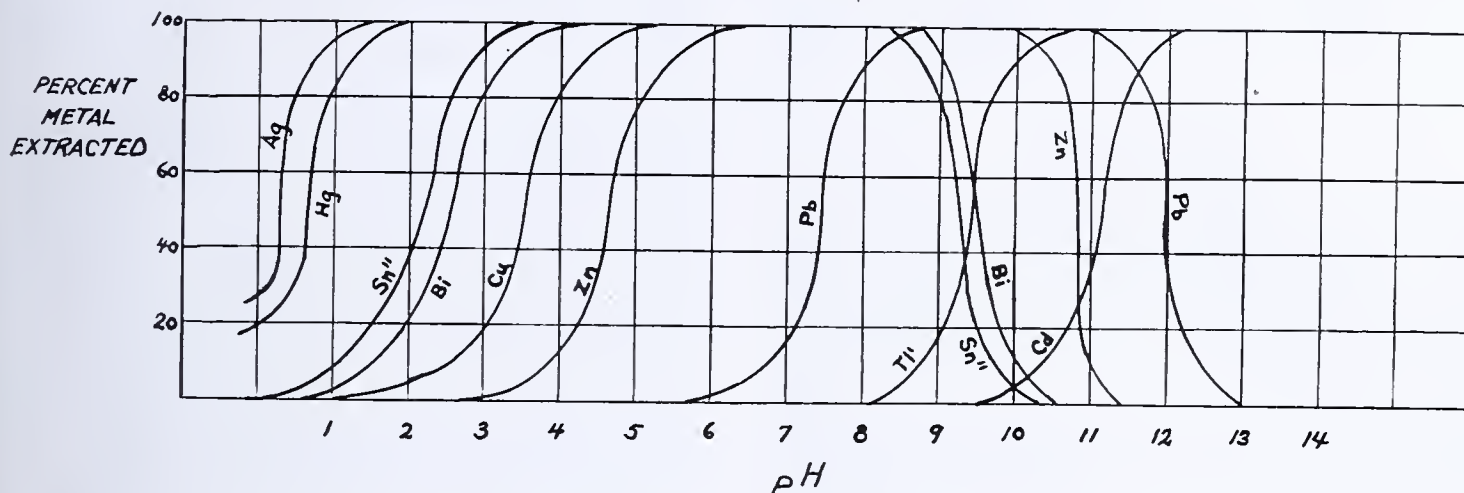


FIGURE 1. PROVISIONAL EQUILIBRIUM CURVES OF SOME METAL DITHIZONATES IN CHLOROFORM

equilibrium curves based on accurate data, the problem of separations in either acid or alkaline solution would be much simplified. The attention of physical chemists is invited towards this interesting problem.

The dithizone system has another string to its bow in the matter of extractions and separations. The second string is the relative stability of other complexes towards the dithizone complex. Citrates or tartrates are used to prevent the precipitation of hydroxides or phosphates when dithizone metals are extracted from alkaline solutions, but do not hinder the dithizone extraction. Fischer and Leopoldi (10) originated the use of cyanides as a discriminative complex former, or masking agent. In weakly ammoniacal solutions the double cyanides of most of the dithizone group of metals are stronger complexes than the dithizone complexes. The exceptions are lead, bismuth, stannous tin, and thallium. Therefore, the last three dithizonates are coextracted with lead dithizonate from cyanide solutions and interfere in the determination of lead. Fischer and his associates (11) also determined that potassium iodide and sodium thiosulfate were excellent competitive complex formers for many of the dithizone metals in acid, but lost this power in alkaline solution. Although the optimum pH for the dithizone extraction of zinc is about 7.0, Fischer *et al.*, nevertheless, were able to develop an excellent method for the determination of zinc by the so-called *Tarnung* (concealment, masking, camouflage) of interfering metals with thiosulfate and potassium cyanide at a pH of 4 to 4.5. Cadmium seemed to be the only metal that gave them trouble, if present in more than 100-microgram quantities. Workers in the United States used thiosulfates and potassium iodide in dithizone methods at about the same time that Fischer did. Winkler (29) and Sandell (23) recommend these reagents in the dithizone determinations of mercury, copper, lead, and zinc. Thiosulfates and iodides in acid solutions will also revert some acid-stable dithizonates and retransfer the metals, now combined in the stronger thiosulfate or iodide complex, from the organic solvent to the aqueous phase. Winkler finds that the mercury-thiosulfate complex can then be readily broken by oxidizing the thiosulfate to the non-complex-forming sulfate, which frees the mercury for a later determinative dithizone extraction.

the extraction of zinc. They then fix remaining interfering metals other than zinc with the carbamate in weak alkaline solution. It seems that under these conditions dithizone becomes almost a specific for zinc, cobalt and nickel being the only metals that will require further study.

Another use of organic complexes in lead determinations has been made in the laboratory of the Food and Drug Administration (3). Iron (ferric iron does not react with dithizone but the ferricyanide formed with potassium cyanide oxidizes dithizone), tin, and about 80 per cent of the bismuth in 100 cc. of acid solution are precipitated by cupferron and then extracted with ether or chloroform, which leaves the soluble cupferrides, including lead, in the aqueous phase. After freeing the lead from the cupferride complex by bromine treatment, it may be extracted later on from ammoniacal solution, separated from residual bismuth, and then determined. This appears to be a very clever short cut to separate almost all the interfering metals from lead in one operation before dithizone is even applied.

There are other complexes besides those mentioned that are, or may become, useful in the dithizone system. A desirable competitive complex in any dithizone determination should have a strong fixing power for as many interfering metals as possible; and little or none for a limited number of other metals including the one that is being determined, diminishing thereby the number that have to be separated by other means. If the pH range for the competitive complex is wide enough to allow separations of the now lesser number of dithizone extractable metals by hydrogen-ion concentration control, an almost specific dithizone method for a given metal may be the result. Another consideration that may govern choice of a competitive complex is the ease with which it may be removed, destroyed, or inactivated when it has performed its mission, and its continued presence becomes embarrassing later on in the determination. A greater number of complexes to select from should promote progress in dithizone methods.

The principle of competitive complexes may find application with other organic reagents. Homologs of dithizone might also alter the picture. Future developments may take unforeseen directions, but the important points that may be



emphasized now, in the separation and isolation division of the dithizone system of analysis, are that the dithizone group of metals can be extracted from aqueous solution and separated from each other by a careful control of hydrogen-ion concentration, by competitive complex formation, or by a combination of these principles. It is certain that physical-chemical investigations of the various equilibria involved could help this analytical problem greatly by enlarging and placing on a firm theoretical basis our present empirical information. Were exact equilibrium data available, dithizone would be a reagent of much greater specificity than it is today.

### Determinations

We now come to the final stage, the actual determination of the metals after they have been extracted from aqueous solution by dithizone and separated, when necessary, from each other. Some analysts, after destroying the dithizone by some form of oxidation or freeing the metal from dithizone combination by extraction with acids, etc., have turned to other than dithizone methods. In the case of lead, the colorimetric lead sulfide method has been much used in Europe. Chemists of the Department of Agriculture have used to good advantage the idea of electrolytic (2) deposition and iodometric titration of the deposited lead peroxide after a preliminary dithizone extraction. Perlman and Menschling (21) in their work on the determination of zinc in maple products and Sylvester and Hughes (24) in England have used dithizone to extract zinc usually contaminated with other metals from aqueous solution, and then determined the zinc iodometrically with ferrieyanide and potassium iodide according to the Lang (17) method, which is said to be specific for zinc. One cubic centimeter of 0.001 *N* thiosulfate is equivalent to 100 micrograms of zinc. The method is, therefore, rather insensitive in the lower range of zinc (1 to 100 micrograms), and this lack of sensitivity must be compensated by larger samples.

Dithizone is readily oxidized, and Hibbard (14) has utilized this property in the determination of zinc after extraction as the dithizonate. He oxidizes the separated zinc dithizonate with an excess of standard bromine in carbon tetrachloride solution and then back-titrates the excess bromine with potassium iodide and thiosulfate. Hibbard believes his results for 10 to 30 micrograms of zinc, in the absence of interfering substances, are accurate to  $\pm 10$  per cent. The determination of other dithizonates can be made in this manner. Hibbard suggests the determination of copper, lead, cobalt, and cadmium. Limiting factors are the purity of the separated dithizonate solutions and the sensitivity of the final iodine-starch titration.

The current analytical methods, based entirely on the use of dithizone, may be classified as extractive titrimetric, or colorimetric (several varieties). Extractive titration methods involve the extraction of metals from aqueous solution at definite pH, and in the presence of fixation complexes when necessary, with successive increments of standardized dithizone solution. The titrations are made in separatory funnels with sufficient shaking between additions to establish equilibrium between the metal and dithizone, and the solvent layer containing the dithizonate is drawn off from time to time, until the green dithizone is no longer changed in color. The intense green dithizone, therefore, furnishes its own end point. The dithizone solution is standardized against known amounts of metal in the same manner.

This principle has been applied to silver and other metals with most excellent results by Fischer *et al.* (13). They sometimes titrate silver, not with solutions of dithizone, but with solutions of copper dithizonate and declare that inter-

ference from other metals is less. They also determine other metals indirectly by a silver titration. In the United States the principle of direct extractive titration has been applied by Winkler (29) to mercury and by Wilkins, Willoughby, *et al.* (27) to lead. The accuracy of the extractive titration methods is of the order of about 1 microgram.

A variation of the above direct titration with respect to lead has been published by Horwitt and Cowgill (15). They extract with excess dithizone, remove the excess dithizone with very weak cyanide solution, revert the lead dithizonate to the equivalent dithizone, and then titrate it with standard lead.

The earliest, and possibly the greatest, success with dithizone determinations has been with colorimetric modifications. Simple colorimetric dithizone determinations developed so far have been of two kinds. They have been described as "one-color" and "mixed-color" methods. In one-color methods developed originally by Fischer and Leopoldi (10) for lead and copper, the metal to be determined is extracted from aqueous solution at the proper hydrogen-ion concentration, with an excess of dithizone in chloroform or carbon tetrachloride solution, and the excess dithizone is then washed from the organic solvent by aqueous solutions of weak ammonia, potassium cyanide, or mixtures of the two. Care must be exercised in the control of the hydrogen-ion concentration of the aqueous wash solution. If it is too high, some of the dithizonate in the organic solvent may partially decompose; if it is too low, not all of the excess dithizone will be extracted, especially from chloroform solvent. In other words, there is apt to be a small compensation of errors that must be duplicated in the preparation of standards and in the standardization of solutions. With the equilibrium curves mentioned previously, the removal of excess dithizone could be made more scientifically than can be done by present empirical means. Fischer originally reverted the dithizonates to the equivalent dithizone by treatment with acids and matched the resulting green colors. Others have used the colored dithizonate itself (30). The sensitivity of various one-color dithizone methods is approximately 1 microgram, which indicates that analysts using them have been successful in balancing one small error against the other.

In the mixed-color methods (1, 6, 25), the metals (lead has been determined more extensively than any other metal in this manner) are extracted from the aqueous solutions at optimum pH with an excess of dithizone in chloroform solution. The excess is not removed, but is allowed to partition between the aqueous and solvent fractions and to modify the color of the extracted dithizonate according to the relative amounts of the metal and dithizone. Thus, in the case of lead, a series of colors from green to red may be arranged with intermediate blues, purples, and crimsons; hence the term "mixed colors." The mixed-color method avoids the sources of error of the one-color methods—viz., incomplete removal of excess dithizone or loss of metal to the aqueous phase. The hue of the unknowns is matched against the hues of a standard series of colors. With a little practice analysts become very expert at matching these hues. The sensitivity is greatest at the ends of the series—that is, where the quantity of metal is smallest and the unchanged dithizone is greatest, and just the reverse. Changing the volumes and concentrations of dithizone in chloroform and viewing the extracts through different column lengths produce different ranges of quantities of metal, but each range exhibits the same progression of hues. Very rapid as well as accurate results may be had in the lead-spray-residue field by using Nessler tubes and viewing the colors transversely. The range of lead determined is from 0 to 200 micrograms and the errors are well within 5 per cent. In this way, 1 microgram of lead has been split into 10 distinguishable parts by extracting it with 5 cc. of a dilute dithizone-chloroform



solution and placing the extract in slim 12.5-cm. (5-inch) vials.

Fischer and his associates (9) have developed another system of mixed-color colorimetry by duplication rather than by comparison with a standard series. They produce the mixed color in the regular way and then duplicate the hue of the unknown in another vessel of the same shape and containing the same volume of dithizone and adjusted aqueous solution, by alternately shaking and titrating into it a standard metal solution. When the hues match, the volume of the standard solution indicates the amount of metal present. Very accurate results are obtained in this manner on 0 to 10-microgram quantities of metal.

These brief descriptions indicate that excellent results can be obtained with simple apparatus. But the analyst can go the limit in the kind of instruments he wants for measuring the transmission, or for comparing the developed colors. The range can be from Nessler tubes to electrospectrophotometers. In the 16 food inspection laboratories of the U. S. Food and Drug Administration a very moderately priced, home-made, neutral-wedge photometer with a special set of color filters has given most excellent service. The neutral-wedge photometer (5) designed by Clifford and Brice is now made commercially. Moderately priced photoelectric photometers using color filters are on the way. A brief description of the principles of photometric measurements as applied to the dithizone colors may, therefore, be of interest.

Fischer and Weyl (12) have given the absorption curves of most of the dithizonates and of dithizone in carbon tetrachloride solution. In the United States the transmission curves of lead, mercury, and dithizone in chloroform have been studied. These data give us the information necessary to make photometric measurements of the pure dithizonates with either spectrophotometers, or neutral-wedge photometers supplemented with proper color filters. In one-color methods the maximum absorption of the particular dithizonate is all that is necessary. In two-color methods a wave length is selected where the absorption of the dithizonate is at a maximum and that of dithizone is minimum, or just the reverse. Under these conditions a maximum "spread" is obtained. If Beer's law is obeyed by both the dithizonate and dithizone colors, the transmissions will increase linearly over the range of metal governed by the concentration of the dithizone. That is, if the densities, or simply scale readings, of the colors produced by standard amounts of metal, read through an appropriate cell length, are plotted against metal, a straight line is obtained. This standardization graph of any given batch of dithizone will remain constant if it is kept free from the oxidative effects of light, heat, or oxidizing agents.

One great advantage of photometric measurement is the avoidance of repeated preparation of standards. If curves for various metal ranges, governed by concentration and volume of dithizone and by various cell lengths, are prepared, the analyst need know only the approximate amount of metal in his unknown to fix the concentration of the dithizone solution and cell length necessary, determine the absorption, and read the result from the proper curve. Photometric measurement so far has been restricted mainly to lead, but its success there indicates its rapid spread into the determination of other dithizone metals. One to 100 micrograms of lead (16, 18) have been determined photometrically in biological material with an error of not more than a few per cent.

#### Purity of Dithizonate Solutions and Accuracy of Results

Dithizone has been criticized for lack of specificity, and all investigators emphasize the importance of separations when

interfering metals are present. The value of the dithizone system of analysis could be enhanced from an entirely different direction if the efficiency of separations made under optimum conditions, discussed previously, could be independently tested by some other method not connected with dithizone extraction to determine possible residual impurities. With the exception of silver and mercury, most of the dithizonates are of various shades of red insufficiently distinct to the eye to serve as a means of detection in mixtures; but they do differ from each other to some degree in spectral characteristics.

Optical methods should, therefore, offer some means for distinguishing dithizonates from each other (26). Clifford (4) has succeeded in reaching this objective in the determination of lead by the use of normal and auxiliary wave lengths or filters. The maximum absorption of the red dithizonates occurs at wave lengths from 500 to 560  $m\mu$  (12). These maxima are so close together that all the red dithizonates will absorb to some degree at any of these wave lengths and the chance for differentiation at any one selected wave length is slight. However, the definite relationship between the absorption of a given amount of a metal dithizonate at different wave lengths is disturbed by the presence of metal impurities with different spectral characteristics. The auxiliary wave lengths or filters must, of course, be so chosen that the disturbing effect of any interfering metal in any given dithizonate will be at a maximum. If the lead analyst finds, for example, that the data obtained on the normal and auxiliary filters are characteristic of lead dithizonate, he can be certain that his final lead dithizonate is pure, or, at the worst, contains bismuth or tin not to exceed a few per cent of the lead determined. On the other hand, if the checks are not satisfactory, serious amounts of bismuth and/or tin contamination are indicated and a repetition of the lead determination with more careful separations is in order.

The additional assurance of the accuracy of the results when the optical check indicates no impurities is well worth the little extra time required to measure the absorption on one or two auxiliary filters. A recording spectrophotometer should simplify this detection of impurities (19). If, in spite of control of hydrogen-ion concentration or complex formation, one or two impurities still persist in appreciable quantity in the dithizonate of the metal being determined, resort can still be had to simultaneous equations based on optical data. How successful such mathematical treatment may be in individual cases remains to be seen. The point to be stressed at the present time is that the introduction of optical transmission or absorption measurements into dithizone investigations may in time furnish a third leg that, with pH control and complex formation, will give a firm support to the dithizone system for the determination of traces of metals.

#### Conclusion

Up to this time the dithizonates of the metals silver, mercury, copper, lead, zinc, and cadmium have received the most analytical attention. The metals bismuth, tin, thallium, cobalt, nickel, and the noble metals, gold, platinum, and palladium have been considered from the standpoint of interferences in the determination of other metals, but investigations designed to develop methods for their dithizone determinations have not been carried very far. Ferrous iron, manganese, thallic thallium, and indium (9) react with dithizone under certain conditions, but their dithizonates are of limited stability and probably of no analytical significance. The field for further investigation is still wide open. Improvements and developments in the dithizone system for the isolation and determination of traces of metals may be expected through (1) hydrogen-ion concentration equilibrium



studies, (2) a greater knowledge of competitive complex formations which will facilitate separations, and (3) photometric transmission measurements of the dithizonate colors which utilize to a greater extent the differences in their spectral behavior.

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# Spectrophotometric Methods in Modern Analytical Chemistry

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IN SPITE of the title of this paper, it is not meant to imply that spectrophotometric analysis is a new invention. Sixty-five years ago the first book on the subject by Vierordt (56) was published in Germany, but little application of its advantages has been made until recent times. It should, therefore, be proper to review briefly the scope, principles, and advantages of the subject in order to justify its use in place of the simpler methods of ordinary colorimetry; for we must look upon spectrophotometry chiefly as an advanced development in this field.

## Definition of Subject and Terms

The term "spectrophotometry" has been defined by a committee of the Optical Society of America (47) as the measurement of relative radiant energy as a function of wave length. The energy may come directly from an emitting source or may be transmitted, absorbed, or reflected by absorbing materials. With few exceptions, the analytical chemist is interested in the measurement of light absorbed by a liquid or gas, and it is to this application of the methods that this paper will be chiefly devoted.

It is fair to assume that some readers are not familiar with the precise definition of certain terms commonly used in spectrophotometry. Chemical spectrophotometry has been a kind of no-man's land between chemistry and physics, and a vast entanglement of conflicting designation has grown up which seems more characteristic of the American than of the English or German literature. It is really necessary for any person writing on this subject to define his terms explicitly; so this paper first reviews those which will be used most frequently and by whose use ambiguities may be anticipated. "Colorimetry," for instance, needs no definition

for an analytical chemist, yet it is used by the physicist to mean "trichromatic colorimetry," something quite different.

The fundamental relation used in these measurements is the Lambert-Beer's law which is illustrated in Figure 1. It is expressed by this relationship (53, p. 18):

$$\log \frac{I_{\lambda}}{I_{0\lambda}} = -k_{\lambda} cl$$

Spectrophotometry is a branch of physical chemistry sorely neglected by the analytical chemist. Its advantages lie in the elimination of comparison solutions, the direct calibration of an instrument by a few simple measurements, the ability to determine independently the constituents of a mixture of colored substances, the precise evaluation of the errors of a method, and the extension of measurements to the invisible regions of the spectrum. Speed is an advantage of colorimetric analysis not lost in spectrophotometric analysis. A brief résumé is given of the various types of instruments available, the important errors and limitation of the present methods, and finally examples of the results which may be obtained with actual analytical problems.



where

$\frac{I_{\lambda}}{I_{0\lambda}}$  = percentage of light transmitted at wave length  $\lambda$  = transmission at wave length  $\lambda$

$k_{\lambda}$  = molecular extinction coefficient for wave length  $\lambda$

$l$  = thickness of cell (in centimeters)

$c$  = concentration of solution contained in cell (in moles per liter)

For any wave length and any given system the value  $k$  should be constant at all dilutions and all thicknesses of absorbent. The constancy of the molecular extinction coef-

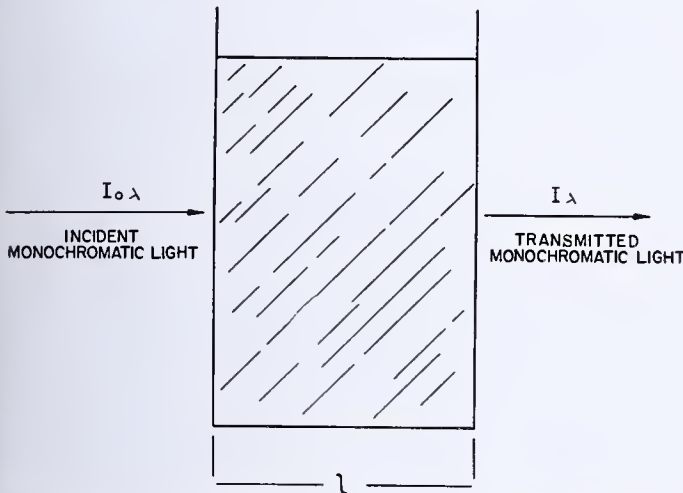


FIGURE 1. CELL CONTAINING LIGHT-ABSORBING MEDIUM

ficient is a criterion of adherence to Beer's law. For actually applying this test, a plot of the extinction coefficient against concentration is more convenient. This and certain other terms are defined as follows:

$$D_{\lambda} \text{ (density)} = \log \frac{I_{0\lambda}}{I_{\lambda}} = E_{\lambda} \text{ (extinction)}$$
$$= k_{\lambda}cl$$
$$\frac{D_{\lambda}}{l} = k_{\lambda}c = K \text{ (extinction coefficient)}$$

Only those terms which will be used are included. Density,  $D$ , is directly proportional to the concentration of a solution (or gas) and to the cell length, and the substitution of density for the logarithm of the reciprocal transmission eliminates negative signs; so there are real practical advantages in the use of this term. The term extinction,  $E$ , used mainly in the German literature, is a synonym. The extinction coefficient is the extinction or density for a centimeter layer of absorbing medium and is directly proportional to the concentration of a solution, if Beer's law holds.  $K$  and  $c$  are the variables in this equation;  $k$  is constant. Beer's law may be valid for colloidal solutions as well as true solutions and some interesting applications of these will be found in the methods referred to at the end of this paper.

Given a method for measuring the density of a solution at a given wave length, we can obtain constant  $k$  by measurements on known solutions—the length,  $l$ , may be obtained by direct linear measurement. Then, to determine the concentration of an unknown, we measure only the density of a layer of known thickness, and we can calculate the concentration of the solution. It is worth while noting that once a calibration curve is obtained on an instrument further “reference standards” are unnecessary. The number of measurements necessary to obtain a curve may be only one, two, or three, depending on how well the particular method has been investigated, and whether it conforms to Beer's law. The manganese calibration which is shown below is easily reproduced (44) and can be obtained with a minimum of measurement. Furthermore, the same straight-line calibration

can often be made at high concentrations and extrapolated to low ones. There is no loss in speed over colorimetric methods and, since standards and comparison solutions are generally eliminated, the methods of spectrophotometry are usually faster.

Application of Beer's Law

Using the extinction coefficient as defined in the last equation, really the density of a centimeter layer of solution, and plotting this extinction coefficient against the concentration of a solution, we obtain a straight line as shown in Figure 2.

These values were obtained by measuring, for light of three different wave lengths from the mercury arc, the extinction coefficients of a series of copper sulfate solutions in approximately 1.2 N ethylene diamine. This represents a considerable excess over the amount required to form the violet copper complex with this base. Each straight line represents the extinction curve for a different wave length of light.

In Figure 3 is represented a plot of the logarithm of the molar extinction coefficient against the wave length of light for the same copper ethylene diamine (34, 50). The highest point on the curve represents the greatest absorption of the solution and is very close to 546 mμ. The absorption at 578 mμ is slightly less and the absorption at 436 mμ is least of all. Referring to the plot of extinction against concentration,

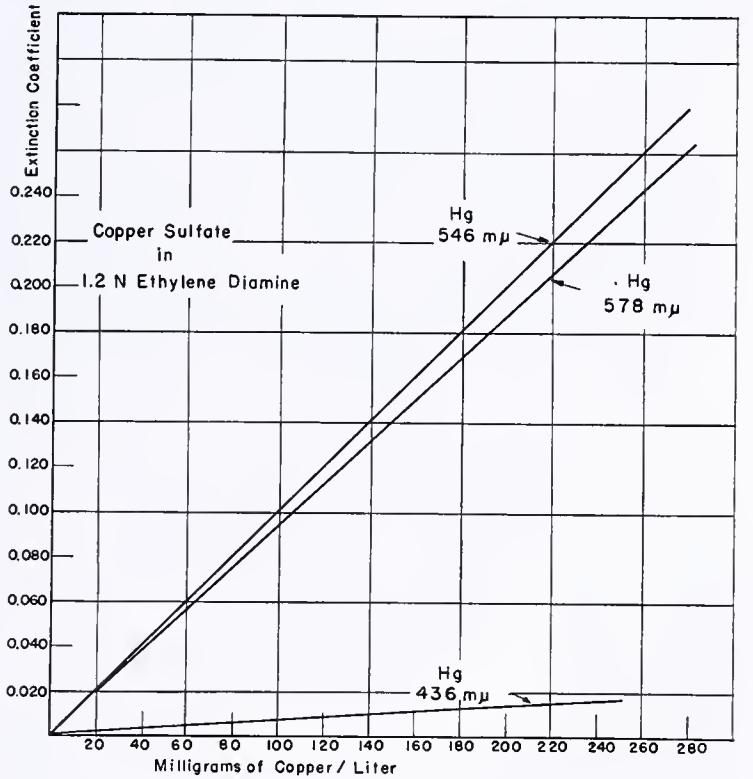


FIGURE 2

it is obvious that we can measure the concentration most accurately when we have the greatest slope to our curves and this is the curve taken at the highest degree of absorption. That this follows from simple mathematical operations can be shown thus:

$$K = kc$$

Differentiating

$$\frac{dK}{dc} = k$$

Or the largest change in density (extinction coefficient) of the solution will be obtained for a given change in concentration, when the extinction coefficient is greatest. This, of course, is at the maximum of the absorption curve.



## Visual Sensitivity and Colorimetry

According to the Weber-Fechner Law (23), the eye is able to detect a 1 per cent change in brightness except at very high or low intensities. When we wish to determine concentration by changes in brightness level, we should attempt to secure the greatest percentage brightness change for a given change in concentration. In comparing the colors of solutions in ordinary chemical colorimetry, we are using the light transmitted, which is largely derived from the regions of the spectrum where the solutions absorb the least. Consequently the percentage change in light intensity must always be less than when we use the maximum of the absorption band.

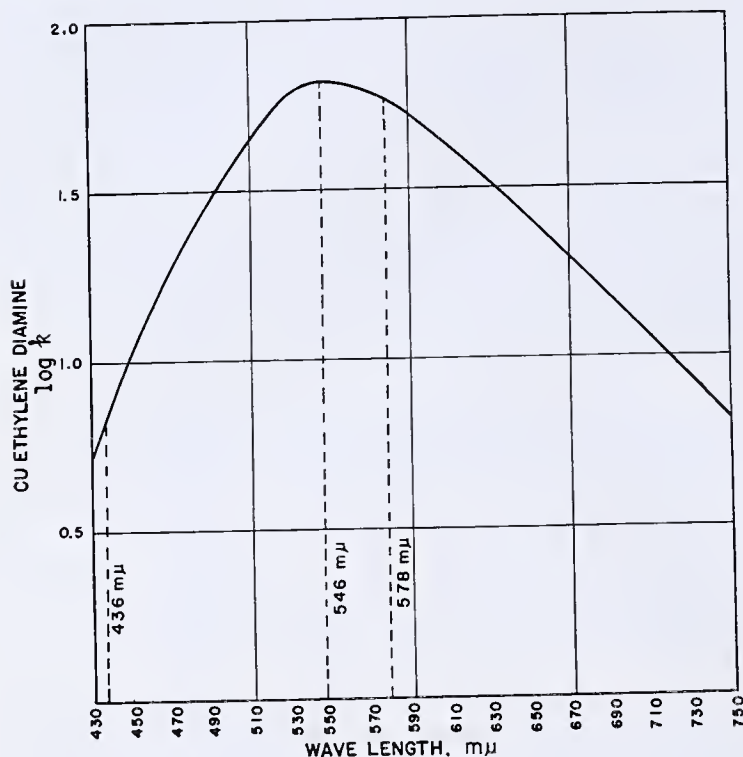


FIGURE 3

The copper ethylene diamine solutions can be used to illustrate this point (Table I).

If we use a nonselective receiver such as a thermopile, the differences will be as shown in Table I. The green light is absorbed almost twice as much as the white light (columns 1 and 2). The difference in the absorption increases rapidly with the difference in concentration (column 3). The eye, however, is more sensitive to the green where these solutions absorb the most, and as a consequence would be better able to detect these differences than the figures would indicate. But the limit that the unaided eye can approach and would only be reached if the eye were sensitive to the wave length 546  $m\mu$  alone, is the difference shown when absorption is measured by the mercury green. Of course, the case for colorimetry is much worse if absorption takes place mainly in the violet as with chromate solutions, because here the decreased sensitivity of the eye to violet operates against the discrimination of small differences in intensity. How greatly the sensitivity of the eye decreases in the violet can be seen by a reference to standard values of relative visibility (27, 48). An interesting illustration of this difference is provided by a comparison of three methods for determining copper which will be discussed below.

### Evaluation of Errors

This brings us to an important phase of quantitative analysis which does not always receive the attention it deserves,

partly, no doubt, because it is not always easy to treat—the evaluation of errors. An important advantage of spectrophotometry over colorimetry lies in the fact that we are able to make very precise comparisons of the most difficult feature in colorimetry—namely, the relative precision and absolute accuracy of determining colors or the degree of absorption of a solution (54). In general we may classify the errors of spectrophotometry by saying that they are of three main classes:

1. From the instability of the absorption of the solution. Some colors are stable, others are fugitive. Some may be very readily reproduced, others are never twice alike. All the effects include temperature coefficient of color change, rate of mixing, etc. The determination of nickel as nickelic dimethylglyoxime, discussed below, is an example of the unstable type, whereas the determination of manganese as permanganate by the periodate method demonstrates a color formation which seems to be stable indefinitely.

2. From the accuracy with which the stratum of solution may be determined. The measurement is linear and can usually be made better than the density reading by the photometer.

3. From the accuracy with which the density reading may be made. There is an optimum density for any particular instrument at which readings can be made. This optimum range can usually be attained by the selection of a suitable stratum thickness. The least error in absolute density reading is usually about  $\pm 0.005$  whether a visual or photoelectric method is used. By a relative photoelectric measurement it is said to be possible to detect changes a hundred times less than this. When densities are too high or too low the accuracy falls off; so we can assume an accuracy of about 0.01 in determining the absolute extinction coefficient.

TABLE I. VISUAL SENSITIVITY

	Light Transmitted Total white light %	546 $m\mu$ (green Hg) light %	Difference for Hetero- chromatic and Mono- chromatic Radiation %
1-cm. layer 1.2 <i>N</i> in Et(NH <sub>2</sub> ) <sub>2</sub> containing: 80 mg. copper per liter 240 mg. copper per liter	91 77	84 57	7 20
Difference for threefold change in concentration	14	27	

The manner in which the precision depends on the absolute density for any given form of instrument is illustrated in Figure 4, which shows a plot of the average deviation in parts per hundred against the density measured. These 99 results represent all of one operator's determinations, including the learning period up to the time these figures were tabulated. A Pulfrich photometer was the instrument used and with it the optimum measurable density is predicted at about 1.0 (61). An error of 0.01 in density would therefore amount to 1 per cent. That experimental results are in harmony with these findings is evident from this plot of points.

### Evaluation of Methods

In Table II is shown a comparison of several colorimetric methods for the determination of copper. The colored compound is indicated in the first column, the wave length at which absorption is determined forms the second column, the change in concentration represented by a change of 0.01 in the extinction coefficient in the third column, and the molecular extinction coefficient in the fourth column. We have already shown that for a given change in concentration the change in density will be greatest for the greatest molecular extinction coefficient. Stated inversely

$$\frac{dc}{dK} = \frac{1}{k}$$

or, in other words, for a measurable difference in density,  $\Delta K$ , the corresponding change in concentration,  $\Delta c$ , which can be determined will be inversely proportional to the molecular



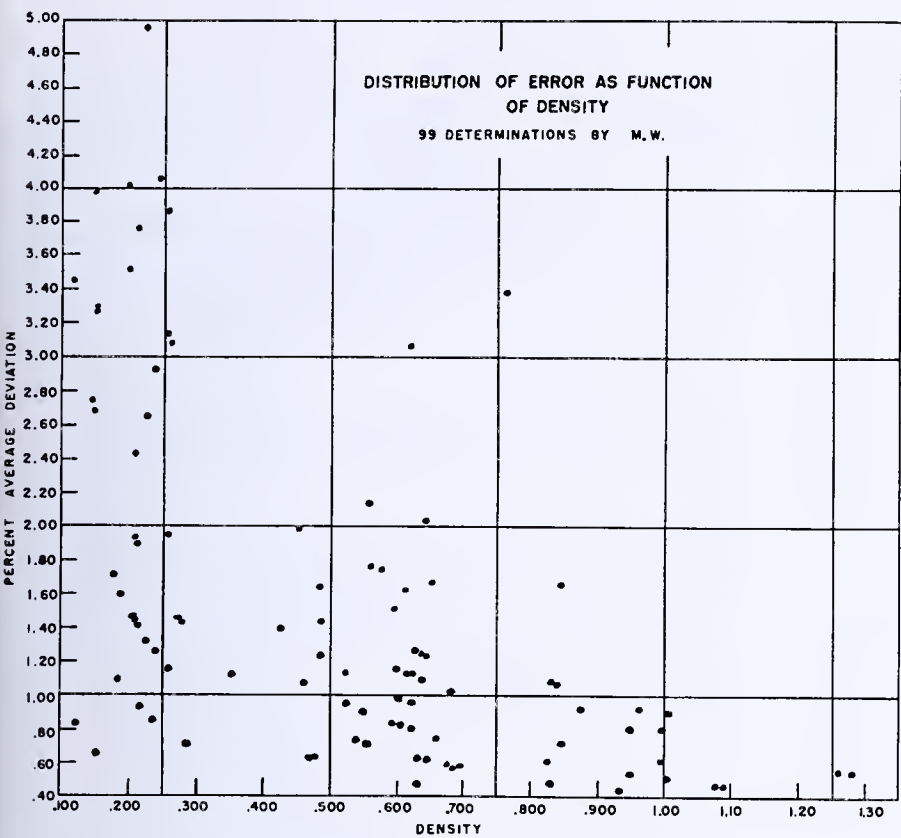


FIGURE 4

extinction coefficient.  $\Delta K$  in the third column is represented by 0.01 unit of density, or the usual accuracy of a measurement. These data immediately eliminate one of the difficulties of ordinary colorimetry. Usually the relative accuracy of different methods is estimated as a subjective reaction of the author and cannot be quantitatively expressed.

TABLE II. COMPARISON OF METHODS

Substance and Method	Region Absorbed, $m\mu$	$\frac{\text{Mg./liter}}{0.01K}$ (1-cm. cell)	$k_{\lambda}(E)$	Investigation
Copper				
NH <sub>4</sub> OH (1.3 N)	578 (Hg)	11.6	54.9	S. E. Q. A. <sup>a</sup>
	610		(53.8)	
Et(NH <sub>2</sub> ) <sub>2</sub> (1.2 N)	546 (Hg)	9.6	66.5	S. E. Q. A. <sup>a</sup>
HCl (28%)	436 (Hg)	1.23	515.	G. A. Smith <sup>a</sup>
Diethyl-dithiocarbamate <sup>b</sup>	430	0.113	531.	S. E. Q. A. <sup>a</sup>
Dithizonate <sup>b</sup>	508	0.0292	21,800. <sup>c</sup>	Liebhafsky and Winslow (36)
Chromium Chromate	436 (Hg)	1.7	313.8	Halban and Siedentopf (20, 32)
	366 (Hg)	0.12	4,416.	
Iron (ous)				
o-Phenanthroline	508	0.051	11,050. <sup>c</sup>	Fortune and Mellon (14)
Manganese Permanganate	546 (Hg)	0.23	2420.	W. Murray <sup>a</sup>
	520		2230.	Müller (44)
	520		2240.	Mehlig (38)

<sup>a</sup> Unpublished data.  
<sup>b</sup> In carbon tetrachloride.  
<sup>c</sup> Calculated.

For instance, in texts on colorimetry, the hydrochloric acid method for copper is said to be "as good" as the familiar ammonia method. Actually (Table III) it is about ten times as good. The deception arises, as has been earlier pointed out, from the fact that copper in hydrochloric acid is yellow in color—the solution absorbs strongly where the unaided eye is least sensitive. If three solutions of the first three reagents of the concentration indicated, each containing copper in the same concentration (say, 200 parts per million), are compared, the over-all density of the violet and blue solutions will appear much greater than that of the hydrochloric acid solution. But not only may the densities of solutions of markedly different hue be misleading, but even solutions of nearly the same color when their relative intensities are compared.

Weigert (58) has described an experiment in which two solutions, both about 0.02 N in copper but one 2 N and the other 13 N in ammonium hydroxide, are compared by daylight in cells 1 cm. thick. The lower concentration of ammonium hydroxide appears darker. When, however, the solution is viewed through a red filter, such as the Corning No. 348 H. R. red shade yellow, the densities are reversed. This phenomenon may be easily explained by an examination of the absorption (58, 59) curves of copper sulfate in solutions of various concentrations of ammonium hydroxide, from which it is seen that as the ammonia concentration increases, the absorption of the solution decreases in the shorter wave lengths where the eye is more sensitive and increases in the longer wave lengths where the eye is less sensitive. Although the increase in the red is much greater than the corresponding decrease, the unaided eye does not detect the difference. When, however, these solutions are observed through a red filter which excludes the shorter wave lengths the true state of affairs is immediately apparent.

Also included in Table II are some other familiar compounds used in colorimetry to provide a basis for comparing the sensitivity of the copper methods.

Range

Spectrophotometric methods may be applied over an enormous range, sometimes with only a single calibration curve.

The data listed in Table II give us the means of calculating the lower limit of concentration we may expect to measure and the accuracy with which we can establish a concentration. Since we may discriminate changes of density of 0.01, we may then expect to be able to detect 29.2 micrograms of copper per liter of solution.

TABLE III. COPPER DITHIZONATE

Cell Cm.	Capacity Ml.	$\frac{\Delta c}{\Delta K}$ when $\Delta K = 0.01$ Micrograms/l.	Copper Micrograms
1	3.5	29.2	0.18
50	300	0.58	0.18
5 (micro)	1	...	$5.8 \times 10^{-3}$

By the use of longer cells than 1 cm., we can detect even lower concentrations. A 2-cm. cell will double the lower limit, etc. As cells are regularly available up to 50 cm., we might set 0.58 microgram of copper per liter as the lower limit of concentration we might reach using the larger cells of about 300-ml. capacity. The absolute amount of copper involved would be 0.18 microgram of copper. The least amount of copper which we might determine is by this line of reasoning equal to about  $5.8 \times 10^{-3}$  microgram, since we may work with microcells which require only 1.0 cc. of solution for a 5-cm. stratum. With photoelectric measurements (53, p. 84) it is possible to measure densities of 0.001 or 0.0001, thus reducing the measurable amounts by factors of 10 and 100.

But these are largely possibilities, as it is doubtful that anyone has yet achieved anything like these limits in spectrophotometric analysis. Liebhafsky and Winslow (36) have pointed out some of the difficulties, largely of a chemical nature, that may be encountered. Kortüm (31) has described the instrumental difficulties which must be watched.



We need not be skeptical, however, of these figures as a temporary goal.

At the other extreme of concentration range, Mehlig (39) has shown that copper may be determined in mattes at concentrations as high as 20 per cent, and data have been obtained for the determination of nickel in steel (45) at concentrations up to 20 per cent with an accuracy of 0.2 per cent. Probably such procedures are entirely beyond the reach of ordinary colorimetry. Calculations based on extinction coefficients of the substances involved may be made to determine when such determinations are feasible, and with what accuracy they may be made. In reactions in which the color develops slowly, Bergami (4) and collaborators have shown how an additional parameter time may be introduced into the usual spectrophotometric equations for first, second, or higher order reactions, making it possible to determine concentration during the time the color is developing.

### Analysis of Mixtures of Colored Substances

Spectrophotometric methods are exceedingly valuable, in that they are selective and permit the determination of each of a series of colored constituents of a mixture. The extinction coefficient at any wave length for a mixture is equal to the sum of the extinction coefficients for each constituent. By simple algebraic processes (53, p. 41) we obtain the following expressions:

$$\begin{aligned} K_{\lambda_1} &= c_1 k_{\lambda_1} + c_2 k'_{\lambda_1} \\ K_{\lambda_2} &= c_1 k_{\lambda_2} + c_2 k'_{\lambda_2} \\ c_1 &= \frac{K_{\lambda_1} k'_{\lambda_2} - K_{\lambda_2} k'_{\lambda_1}}{k_{\lambda_1} k'_{\lambda_2} - k_{\lambda_2} k'_{\lambda_1}} \end{aligned}$$

A similar expression can be obtained for each concentration. We may measure the molecular extinction coefficients,  $k$ , at two different wave lengths, on known solutions. The extinction coefficients,  $K$ , can then be measured on the mixture and the individual constituents determined. More than two colored constituents can be determined when the molar extinction coefficients are known for as many wave lengths of light as there are constituents in the mixture. Weigert (58) has determined as many as four constituents of a solution by this method. Though the accuracy is not high, it is still usable and is beyond the reach of ordinary colorimetry. Pinsl (49, 62, p. 63) has developed a method for the simultaneous determination of titanium and vanadium in steel by measurement of the absorption of the two mercury lines, 436  $m\mu$  and 546  $m\mu$ , by a suitably prepared solution.

A simple case of mixed absorption occurs when the molecular extinction coefficient of one constituent approaches zero, but the other constituent absorbs appreciably at some particular wave length. A practically important instance of this type is provided by ferric salt solutions. It is frequently possible to develop a colored compound of manganese, molybdenum, chromium, phosphorus, etc., in a solution of a steel sample, but it is not always easy to compensate by simple colorimetry for the presence of iron. Ferric ions and ferric phosphate, citrate, and fluoride complexes are light yellow in color—mostly because of the absorption of violet light. It is possible, for instance, to form colored nickel complexes in solution with absorption bands where the ferric salts transmit and hence allow the determination of nickel independently of the iron (45). The fact that at zero concentration the calibration curve obtained passes through zero extinction indicates that the yellow iron citrate complex is practically 100 per cent transparent at about 530  $m\mu$ .

Permanganates show a similarly strong absorption in the green and are another instance when this phenomenon may be useful (38, 44, 45). A reference to the absorption curve

of the permanganate (32) ion shows that its maximum lies in the green near the mercury line 546  $m\mu$ . In the author's laboratory a single calibration has been found usable over a 200-fold range—from about 0.01 per cent to about 2.0 per cent and probably even higher (Figure 5). The permanganate color is likewise characterized by great stability when developed by the procedure of Willard and Greathouse. It is also interesting for those who are prone to discount the reliability of Beer's law that the absorption curve is very little affected by the cations with which the manganese is combined (41).

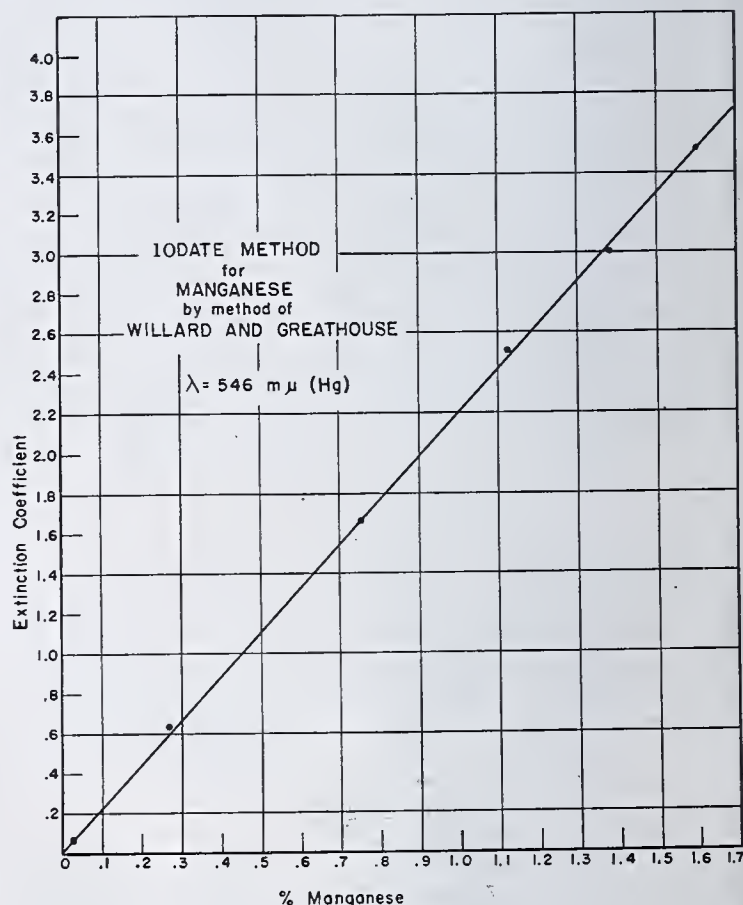


FIGURE 5

Finally, even if we have a mixture of two constituents of the same color, we may, if one is known or remains constant, correct for it or obtain a calibration curve of the type reported by Murray and Ashley (45). Phosphorus may be determined in steel by the conversion of phosphoric acid to a phosphovanadomolybdic acid, which possesses a strong yellow color. This reaction may be carried out directly on a nitric acid solution of the steel sample and the calibration curve reveals that at zero concentration of phosphorus the ferric nitrate has a marked absorption. The point at which our calibration curves cut the vertical axis shows the degree of absorption in each case. It can, however, be made to yield results comparable to those of the standard volumetric method using the molybdate complex. This method has not been generally used and has always been considered of low accuracy—mainly because of the difficulty of matching yellow solutions by ordinary colorimetric methods.

### Hydrogen-Ion Determination

The determination of hydrogen ions is a special branch of chemical analysis with tremendous practical importance. It is carried out by the use of either potentiometric or indicator methods. Although potentiometric methods have much to recommend them from convenience, they are subject to some very serious limitations especially when used on unbuffered



solutions. The use of indicators, on the other hand, is generally applicable except in very highly colored or very turbid solutions, and the spectrophotometer doubtless provides the most precise means of using indicators. Indicator action is usually characterized by the existence of a substance in two forms, either or both of which may be colored, and whose equilibrium relationship depends on the hydrogen-ion concentration of the solution in which they occur. If one form only is colored, the degree of conversion is easily ascertained by measuring the density with a spectrophotometer. Knowing the concentration of the indicator, it is easy to calculate from the molecular extinction coefficient the hydrogen-ion concentration.\* This is usually done by forming a calibration curve for a given concentration of indicator by the use of buffers of known pH, and converting the density reading directly into pH.

When both forms of the indicator are colored, the concentration of each form may be ascertained either by the first method or more accurately by comparing the relative intensities of the absorption bands produced by each form of the indicator. The intensity ratio of the two absorption bands will be independent of the total concentration of the indicator over wide ranges of concentration, and this ratio may be used directly for determining the pH. Since the purity of indicators is variable and it is not always easy to reproduce low concentrations accurately, we have a decided advantage in the use of these two-color indicators. This was first pointed out by Holmes (25) in 1924, and since then has been applied by several investigators. Brode (6) and Fortune and Mellon (15) have published interesting and useful families of curves showing the growth and decay of these absorption bands as the pH is changed. Hähnle (19) has recently shown that a linear relationship exists between the logarithm of the ratio of the intensity of these bands and the pH.

### Spectrophotometry in the Infrared and Ultraviolet

So far this discussion has been implicitly applied only to materials absorbing in the visible spectrum. Actually, materials absorbing in the infrared and ultraviolet may also be determined by the principles already outlined, but the technique involved is considerably different for each. Although many successful specific applications have been made, this review must be confined to a few interesting cases merely to demonstrate their usefulness. Many of these invisible absorption bands are of extraordinary intensity and may be more characteristic than the color of permanganate.

Carbon dioxide is one of these substances and McAlister (37) of the Smithsonian Institution has constructed an apparatus for the continuous determination of carbon dioxide in plant respiration experiments based on this principle. It depends on measuring the degree of absorption of a band at 4,200 to 4,300  $m\mu$  in the infrared which is specific among gases for carbon dioxide. The band is isolated by a spectrograph serving as monochromator and the degree of absorption of the radiation is determined by a thermopile. This arrangement allows the determination of 1 p. p. m. of carbon dioxide in about 5 seconds. The period of the galvanometer is the limitation on speed and can be greatly decreased. This represents a percentage of 0.0002 to 0.0005 per cent of carbon dioxide per scale division. Similarly Warburg and Leithauser (57) determined ozone, nitrous oxide, and nitrogen pentoxide in the presence of one another and nitrous oxide in the presence of nitrogen tetroxide. Ammonia, water vapor, chloroform, and many other vapors show strong infrared absorption which might be used for their determination.

Benedict and collaborators (3) have carried out the analysis of deuteromethanes and ethanes by means of infrared

absorption spectra. Solutions are also open to infrared investigation. Errera (11) has recently determined traces of moisture in other solvents by the absorption of a band attributed to dissociated water in concentrations less than 0.050 per cent.

The detection of mercury vapor by its absorption of the 2,537 Å. resonance line from a suitable mercury lamp is the most outstanding commercial application of spectrophotometry in the ultraviolet region of the spectrum. One part of mercury vapor in 100,000,000 parts of air is the sensitivity of this instrument (1). Carr (7) reports that among the organic compounds benzene is as easily detected in the Schumann region at 1,732–89 Å. as mercury. Benzene cannot be used even to wash stopcocks in the supplementary apparatus without leaving traces that can be identified for days after. Absorption spectrophotometry has been used in various ways for the identification and determination of vitamins A and C and innumerable other organic products (53, p. 26).

A considerable advantage could often be gained by transferring measurements usually made in the visible region of the spectrum into the ultraviolet. The well-known colorimetric determination of chromium is an example of this. The absorption of chromates rises steeply, going from violet to ultraviolet, and is at a maximum at about 366  $m\mu$  (33). The actual advantage to be gained by a change from 436  $m\mu$  to 366  $m\mu$  is a fourteen-fold increase in absorption.

### Construction of Instruments

The development of the usefulness of the spectrophotometer has been a direct result of the efforts of the instrument maker. Even to mention all the instruments made would be extremely difficult; this paper merely discusses a few that are typical to illustrate the means of operation. First, however, a little of the theory involved in the measurements will be covered.

As the name implies, the spectrophotometer does two things—it selects a portion of the spectrum, and then measures the intensity of the light selected by means of a photometer. Practically, we cannot usually do better than to select as narrow a band of wave lengths as possible. In general, there are two methods in use for doing this—by filters, or by a monochromator. If either is used with a continuous source of light, the purity of the light separated is not very great, but the monochromator gives purer radiation—that is, a narrower band of wave lengths—than the filters. The band of radiation from the filters may be 250 Å. in width and less. Usually the purity of the spectrum entails a sacrifice in the intensity of light transmitted, and one must arrive at a compromise of these two factors. By using a discontinuous source such as a mercury arc and suitable filters or monochromator, light of high intensity and high purity may be obtained for the lines available (47, p. 185). However, the lines are not always where you want them, and the arc has a background which detracts from the purity of the light. The lines are frequently complex and it is only the exceptional lines which attain a true monochromatic purity.

It is customary to call photometers with a system of filters "absolute colorimeters," and the measurements made with them "abridged spectrophotometry" in order to differentiate them from the instruments employing prism monochromators which give more accurate results. Since it is merely a difference in the breadth of the band which is taken for a determination, the distinction appears artificial. The fact that a selected portion of the transmitted light is examined is the essential difference between the spectrophotometer and the colorimeter, and the instrument with filters consequently is more like a spectrophotometer than a colorimeter. Probably no one will question that the results obtained with the



simpler forms of instrument can be done at least as well with the more complex. Most of the absorption bands with which we deal are broad, such as those of chromates and permanganates, and if the measurement is made at the peak of a band, excellent results may be obtained. If, however, the measurement must be made at the edge of a band where the absorption is changing rapidly, the different portions of the light transmitted by the filter are absorbed to a different degree with the result shown in Figure 6.

The dotted line represents the transmission of a violet filter with a peak transmission at 430  $m\mu$ . The solid lines represent the absorption of a yellow solution at different concentrations. Since the lines cross the filter unsymmetrically, the chromaticity or color of the light through the filter varies and makes matching very difficult or impossible. In such cases Beer's law will not hold for the measurements. This effect may be apparent to a lesser degree with a monochromator, depending on the slit widths used.

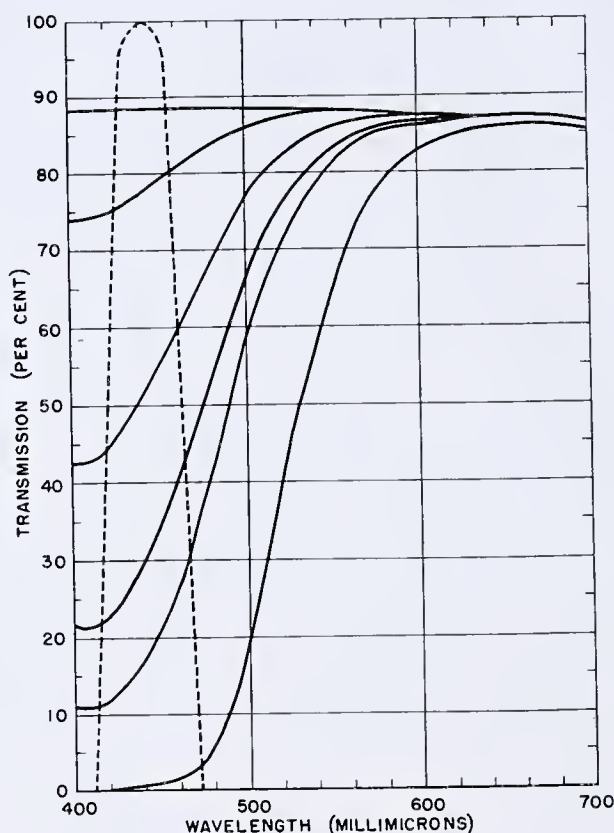


FIGURE 6

Solid filters are usually of glass or gelatin. The gelatin filters almost invariably show a high transmission to the longer wave lengths beyond 7,000 Å., which can be blocked by the use of suitable glass filters or a copper sulfate solution. Although colored glasses of various sorts are widely manufactured, almost the only ones suitable for the purposes discussed above are the Corning glass filters (9), and the Jena glass filters (12) supplied through the Fish-Schurman Corporation. The Eastman Kodak Company (10) markets a large number of filters, almost all of which are of gelatin mounted in glass. These manufacturers all supply literature describing the stability, transmission curves, etc., of their filters. An unusual combination for 560  $m\mu$  is that by Gibson (17).

Liquid filters may be employed in some instruments and may be prepared according to a large number of recipes (5, 30, 59).

It is frequently possible to devise filters for specific purposes by a reference to the Atlas of Wood and Uhler, or absorption curves in such tables as the International Critical

Tables or the Physikalisch-Chemische Tabellen of Landolt-Börnstein.

It is not possible to describe the various forms of monochromators in detail, but one may summarize them by saying that they operate on the principle of the dispersion of light as does the spectrograph. The materials of which they consist depend on the region of the spectrum in which they are expected to operate, and the degree of performance that is expected of them. An interesting application of chromatic polarization in a monochromator is described by Öhman (46), though it has not come into any general use.

The photometer for the visual region of the spectrum may consist of a differential device adjusted by the eye, or a thermopile, photoelectric receiver, or photographic arrangement which may also be used in the ultraviolet or infrared region of the spectrum. It is not possible to do more than review briefly the methods used in the visible spectrum as being typical of the technique involved. Discussions of infrared methods will be found in a paper by Barnes and Bonner (2) which appeared last year. Kortüm (31) also gives a useful review of the methods and difficulties involved in absorption spectrophotometry in the ultraviolet. An interesting instrument has been constructed by Hogness and his co-workers (24) at the University of Chicago.

The various forms of photometers commercially available will be of most interest to the chemist who is going to use spectrophotometry as a tool in other work.

Some of the many forms of photometers have been described by Gibson (13, 16), Weigert (59), Mellon (40), and Twyman and Allsopp (53). A short summary of instruments adapted to the methods discussed in this paper will be given in order to illustrate the different types of instrument available. Further details can be obtained from the individual manufacturers.

The Zeiss Pulfrich photometer, the progenitor of the "absolute" colorimetric type of instrument, has been frequently described in the literature. It usually employs two absorption cells, in one of which is placed the material investigated and in the other a blank. Two beams of light of equal intensity from an incandescent lamp pass through the cells and may be observed simultaneously through an eyepiece as a circular divided field. Twelve filters contained in the eyepiece enable one to isolate bands about 25  $m\mu$  wide at distributed intervals through the visible spectrum. The absorption of the unknown is compensated by reducing the intensity of the unabsorbed beam by means of a variable aperture in the objective. When the two beams are of equal intensity, the amount of absorption can be read from a calibrated drum either as extinction or percentage transmission. A mercury lamp may also be used in conjunction with special filters and the three wave lengths 436  $m\mu$ , 546  $m\mu$ , and 578  $m\mu$  can be separated.

The Leitz instrument "Leifo" is similar in equipment but uses polarizing prisms to vary the intensity of the light instead of apertures. The Aminco wedge photometer is also similar to these instruments but varies the intensity of light by means of a calibrated neutral wedge. The Bausch & Lomb spectrophotometer employs an elaborate arrangement of crossed Nicol prisms for varying the intensity of the two light beams. The two beams pass from the photometer through the monochromator which takes the place of the filter and may be adjusted to give a narrow band of wave lengths at any part of the spectrum. In principle this instrument is similar to the König-Martens and Hilger-Nutting spectrophotometers. These instruments are the most highly developed of those employing visual adjustment.

Instruments employing photoelectric or barrier-layer cells instead of the eye have come into general use and almost every chemical supply house has one of these on the market. Though the simpler forms of these instruments are not usually called spectrophotometers, they can be converted into a cruder form of the instrument by the use of filters. Gibson has pointed out (16) that the name "colorimeter" is just as inappropriate except under very special conditions.

The photometer, an instrument manufactured by the Central Scientific Company, shows the use of a barrier-layer cell to read light intensity directly. It consists principally of a lamp, variable diaphragm, lens, absorption cell, filter and barrier-layer cell,



and microammeter. Readings are taken with and without solution under investigation in the absorption cell and the concentration is determined by calibrating the meter reading with the percentage composition.

Differential instruments employ two barrier-layer or photoelectric cells illuminated by a common light source and balanced to zero current against one another with and without an absorbing solution in place by changing the light on one cell or by a slide wire bridge. Instruments of this type are the Lange Universal photoelectric colorimeter, the KWSZ photometer, the Hilger absorptiometer, and the Aminco photometer.

Finally, the General Electric Hardy recording spectrophotometer comprises an entirely automatically operated monochromator and photometer with a recording mechanism which draws a graph of transmission *vs.* wave length between 400  $\mu$  and 700  $\mu$ . Very complete descriptions of this instrument are given by Michaelson (42, 43), Hardy (21, 22), and Gibson (18).

## Reactions and Methods

It follows from what has been said that any colorimetric method can be used for the methods described. Excellent compendia of these have been provided by Yoe (60) and Snell (51) and specialized books have appeared (55, 62, 63), and descriptions of clinical methods (63). Potential material can easily be found by an inspection of the spectral absorption curves in International Critical Tables, Landolt-Börnstein's "Physikalisch-Chemische Tabellen," Coblenz's "Investigations of Infra-Red Spectra" (8), and LeComte's "Le Spectre Infrarouge" (35). Many useful reactions are described by Strafford (52) and in the recent "Tables of Reagents for Inorganic Analysis" (26). Werner complexes because of their nonionic character are especially adapted to the methods discussed but have been exploited to only a limited degree. The *o*-phenanthroline ferrous complex mentioned in Table II is an example of this type of compound. Its stability and indifference to large changes in solution environment are demonstrated by Fortune and Mellon (14).

The density of many colloidal solutions may be photometered and, when their adherence to Beer's law is not sufficiently close, calibration curves can be constructed to convert densities into concentrations. The determination of low concentrations of phosphorus in steel by the development of a turbid solution of strychnine-phosphomolybdate has been worked out by Koch (29, 62), and the determination of nickel, copper, and cadmium by Juza and Langheim (28).

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# Present Status of Colorimetry

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**I**N THE current literature of optics and analytical chemistry the term "colorimetry" may have quite different meanings for different individuals. To the physicist it implies measurement of color in the sense of determining the magnitude of the three attributes, hue, brightness, and purity, or of the tristimulus values, red, green, and violet (48). His interest might be considered as color analysis. To most chemists colorimetry generally implies measurement of the amount of a constituent by comparison of the colored system containing the unknown with a similar system containing a known amount of the desired constituent, or with a system visually equivalent to the latter. In this sense the chemist's colorimeters are really only comparators. There are, of course, other methods of measurement.

It is the author's hope that this presentation will serve to correlate, at least from the viewpoint of analysts, the interests of both the physicist and the chemist in the problem of the measurement of colored systems. Limitations of space restrict the material to little more than an outline of the items concerned.

## The Domain of Colorimetry

In its broadest sense colorimetry includes all procedures which have as their objective the measurement of some property related to the color of the sample. Systems possessing the attributes of color comprise everything we recognize as being colored, including solids, liquids, and gases. The outline of methods of measurement given below provides for all such cases. Since the chemist, or at least the analyst, has been most concerned with applying colorimetry to solutions, this discussion is confined largely to systems in the liquid state. In addition, it is limited to quantitative work, as a previous paper (32) covered the general analytical uses of color.

In solutions the solute may be considered as the desired constituent. If such a constituent is to be determined colorimetrically, either it must itself possess suitable colorimetric characteristics, such as those of the permanganate ion, or, as much more frequently happens, it must be capable of reacting with some reagent to give a substance having suitable colorimetric characteristics, such as those produced by an aqueous solution of chlorine reacting with *o*-tolidine.

The extent to which quantitative methods have been based on the colorimetric properties of such systems is shown in the treatises of Yoe (53) and of Snell and Snell (41). The latter work, comprising two large volumes, includes over 900 methods in which approximately 700 different reagents are used for nearly 400 elements, radicals, and compounds (40). Much material of general interest concerning colorimetric methods of analysis is summarized in these treatises. In 1936, for the first time, a special section of the *Annual Reports of the Chemical Society* (43) was devoted to colorimetry. Many papers are appearing each year to increase our knowledge of this field. The dates of the references cited here reflect the

**In reviewing the present status of colorimetry attention is directed especially to the importance of colorimetric methods of measurement as revealed in current periodicals and two comprehensive treatises; the variety of applications already made, together with the general limitations of such measurements; and a classification of the kinds of methods available for making colorimetric measurements, including suggestions for a consistent usage of terms.**

present interest in such work. Incidentally, this wealth of material seems to justify the conclusion that the time has arrived for elementary books in quantitative chemical analysis to divert a little attention from gravimetry and titrimetry to colorimetry.

The range of sensitivity of the methods is highly variable. It is not possible to generalize, because there are methods which are sensitive to one part per billion (an exception, of course),

and others applicable only to 10 to 20 parts per million (also an exception). Most methods are applicable over a range from about 0.5 to 10 p. p. m. The range of application is determined by the intensity of the color of the system to be measured and by the sensitivity of the means of measurement used. With very low and with high concentrations of the desired constituent small differences in amounts cannot be determined reliably. Such methods usually are not applicable, without dilution, to quantities greater than 1 per cent of the total sample, although, using a spectrophotometer, Mehlig worked with much larger amounts (28). The absolute accuracy differs for different methods of measurement. With visual comparators it is usually within 5 per cent. Well-designed photoelectric instruments, on account of their increased sensitivity, give a somewhat lower error.

Colorimetric measurements can be applied to a wide variety of systems. In recent years there has been a large number of papers in biochemistry on the application of such procedures, with methods for the clinical laboratory predominating. However, one finds colorimetric methods applied to industrial products ranging from foods to steels—in water analysis, for example, they have long been official for certain constituents.

## Methods of Measurement

Many chemists are probably not fully aware of the number and the variety of devices which have been proposed for measuring different characteristics of colored systems. The last two decades have brought notable advances in the introduction and improvement of such instruments. All the apparatus is based essentially on the measurement of a systemic property (31).

The résumé following is intended to be an outline of the most important kinds of instruments now being used for colorimetric measurements in analytical work. The classification is a modification of that presented recently by Gibson (13) in reviewing the subject from the viewpoint of physics. Specific commercial instruments are mentioned as illustrative of a class rather than as necessarily the best of the type available.

Since the term "colorimeter" is not used in the same sense in physics and chemistry, the author suggests that it be reserved in each field for any instrument that measures a property that is a function of one or more of the attributes of color. Then instruments which have a special application can be designated by more specific terms, as indicated below. Used in the sense proposed, colorimeters would include



spectrophotometers measuring the visual spectrum but not those for the ultraviolet or infrared regions. This is analogous to limiting the term "light" to the visible region, ultraviolet "light" then being a misnomer.

### Stimulimeters

The instruments called colorimeters by physicists will be considered first. Since such apparatus is designed to match, by means of a suitable combination of known stimuli, the stimulus of the system measured, the term "stimulimeter" seems appropriate. All students of optics are familiar with the matching of a given color by means of three rotating disks, colored red, green, and violet, so arranged that the relative amounts of the three "primaries," or stimuli, can be varied until a match is obtained. Different modifications of such devices depend upon the nature of, and the method of combining, the stimuli. (Since it seems probable that one might have stimulimeters, comparators, and absorptometers in other scientific fields, it may be desirable to use the word "color" with each term. We would then have color stimulimeters, color comparators, and color absorptometers.)

In the additive type the observer mixes the primaries or standards in such a manner that the mixture is the sum of the components. Examples of those dependent upon material color standards are the apparatus using Munsell paper disks, and the instruments designed by Donaldson (6), Guild (17), and Newhall (35). In those using spectrum primaries we may distinguish between the trichromatic type in which light of three different wave lengths is mixed, as in the apparatus of Guild (18), Verbeek (49), and Wright (52), and the monochromatic type in which light from a heterogeneous stimulus ("white light") and a small wave length band of the spectrum are mixed. For purples the heterogeneous stimulus is matched by adding the spectrum light to the sample light. The apparatus designed by Priest (37) is an example.

In subtractive instruments the illuminant is passed successively through the standards, each of which absorbs in turn part of the light transmitted by the previous one, until a match is obtained. The standards may be such materials as solutions (4), wedges of dyed gelatin (22) or glass (23), or glass disks as used in the Lovibond tintometer (47).

Of the various stimulimeters the Lovibond instrument is apparently the only one used much by chemists. Even its use is for color specification rather than for chemical analysis, although it is possible to correlate concentration and certain stimulimeter readings. In addition to the difficulty of reproducing the arbitrary filters and of relating their tristimulus values to concentration of solute in a colored system, more important diffi-

culties have prevented general adoption of such apparatus, especially the additive type. Some of the instruments are too complicated for routine work and in all of them the quality of the light source must be carefully maintained and the observer should have both a normal visibility curve and normal mixture data (20). Further information concerning these instruments may be found in treatises on physics or in Guild's papers (15, 16).

### Comparators

In the instruments which should be called comparators the measurement is made by matching the system containing the desired constituent in unknown amount with a similar, standard system containing the desired constituent in known amount, or with something visually equivalent to such a standard. When the desired constituent itself is suitable for preparing the standard, the solution is prepared in permanent form whenever possible. In other cases, in order to allow for compensation of errors, it is necessary to prepare the standard at the same time and under the same conditions as the unknown.

Visually equivalent standards, many of which are permanent, have been prepared from various materials, such as solutions of inorganic or organic compounds, glass, and even color cards. Ordinarily they are recommended for the best work only when it is impossible or inconvenient to use the desired constituent itself for standards. Their spectral transmission (or reflection) characteristics are seldom the same as those of the desired constituent, which renders matching impossible under illuminants of different spectral distributions. The spectrophotometer has revealed (7, 29, 44) notable differences in transmittancy in some permanent standards and unknowns matching them visually under a given illuminant.

Among the many devices which have been made in developing apparatus to be used as comparators three types may be recognized.

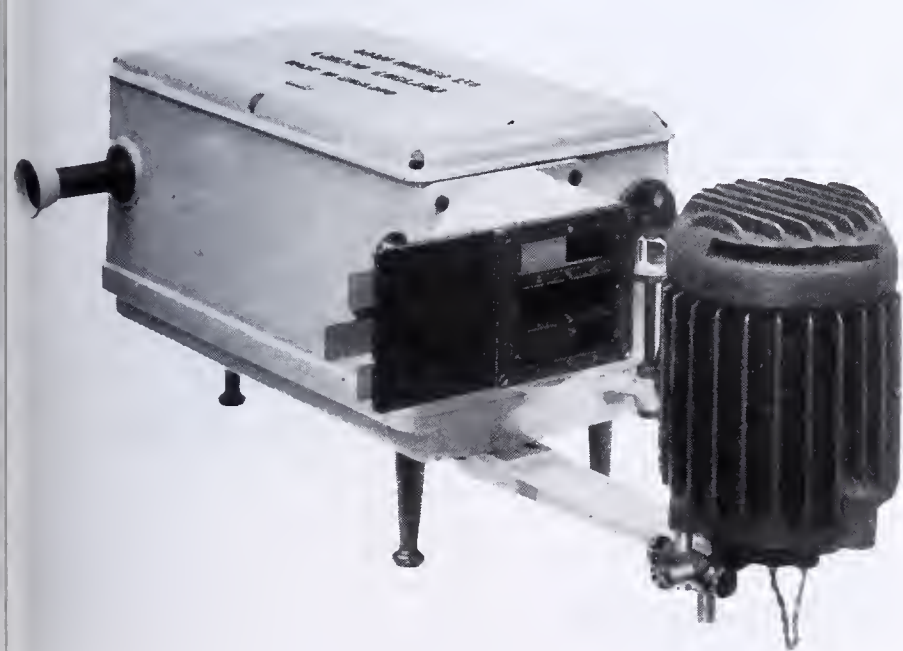
**STANDARD SERIES TYPE.** The old standard series technique remains probably the simplest and least expensive of the widely used colorimetric methods. It is especially desirable for solutions not obeying Beer's law, since the unknown and standards have the same thickness. Solutions or glasses are used most as standards, the matching being accomplished visually. The new roulette comparators facilitate comparison in Nessler tubes, preferably with plane glass bottoms.

**BALANCING TYPE.** Another widely used method consists in comparing the unknown solution with a single standard solution, the depth of one being fixed and that of the other changed until a match is obtained. If the systems obey Beer's law, the concentrations of the desired constituent in the two solutions are inversely proportional to the depths of solution measured. For the many systems not obeying Beer's law the two solutions must have nearly the same concentration, or the necessary correction must be determined experimentally.

The Duboscq comparator is the best known type of instrument used for balancing. Snell and Snell (41) and Yoe (53) illustrate a number of the many variations of design used, practically all made for visual matching. Recently Goudsmit and Summerson (14) made an interesting modification in which the matching is accomplished by means of two photocells.

Thiel (46) has proposed a method which he designates as "absolute colorimetry," based upon determining the specific extinction of the unknown by matching the solution with a gray solution prepared from dyes and having a specific extinction of 0.5. Thiel has published more than fifteen papers on the application of the procedure.

**DILUTION AND DUPLICATION TYPE.** Another type of comparator is based upon matching the known and unknown solutions by means of dilution or duplication of the color. Kolthoff and Sandell (25) refer to duplication as colori-



Courtesy, Adam Hilger, Ltd.

FIGURE 1. DONALDSON TRICHROMATIC STIMULIMETER



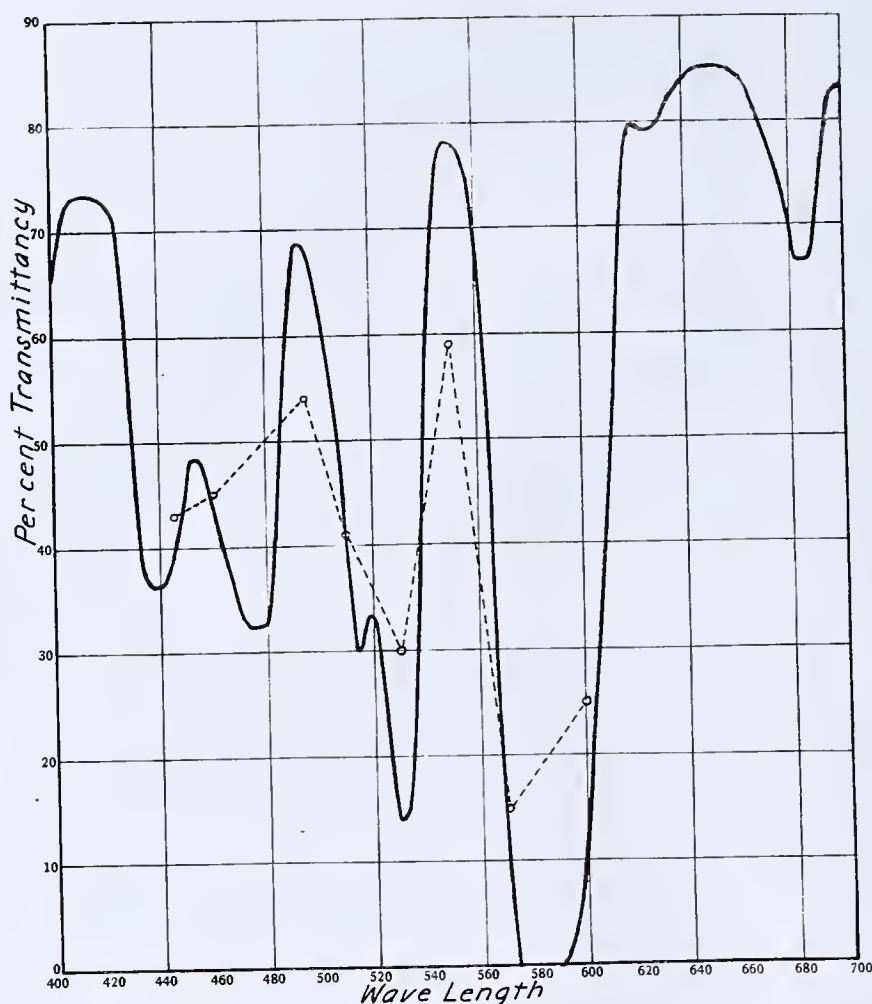


FIGURE 2. SPECTRAL TRANSMISSION CURVES FOR A DIDYMIUM GLASS

Solid curve, with a recording spectrophotometer  
Broken curve, with a filter photometer

metric titration. Although there are commercial devices for this operation, their general usefulness is such that they will not be considered further here. Details may be found in the treatises mentioned above. Matching in Nessler tubes by duplication is recommended in some steel laboratories.

### Absorptometers

The third class of instruments comprises devices which may seem to be too different in nature to justify inclusion in the same group. Essentially, however, they all measure, for a given illuminant, the light-absorptive capacity of the system studied. Since absorption is the property measured, the instruments may be called absorptometers. (For some years the Kipp and Zonen Co. has used the term "absorptiometer," and recently Adam Hilger has adopted it. The spelling "absorptometer" seems preferable, to be consistent with "reflectometer," a term currently used.) Instead of being graduated in terms of absorption, the conventional practice is to use transmission (or something related to it, such as extinction coefficient) for transparent media and reflection for opaque material. Appropriate names for the instruments are transmissimeters and reflectometers, respectively.

**FILTER PHOTOMETERS.** In general, photometers are designed to measure intensity (brightness) of illumination. Those used in colorimetry measure the proportion of light incident upon a system that is transmitted (or reflected). Since all colored solutions absorb some of the incident light, the analyst's problem is to relate the concentration of the desired constituent to the amount of light transmitted.

The solutes in colored solutions absorb light in certain definite regions or bands in the visible spectrum. The variation in transmission with concentration is greatest when the incident light is restricted to the spectral region of the solute's greatest absorption. In photometers this is accomplished, at least partially, by interposing a suitable filter, usually of glass, between the illuminant and the observer, hence, the name filter photometer. Several manufacturers have selected a series of 8 or 9 glasses for which the regions of maximum transmission are fairly well spaced from 450 to 650  $m\mu$ . Such a filter permits the passage of a wide spectral band of light. Selection of the best filter for a given determination should be based on the spectral transmission curve of the solution to be measured. Thus the absorption band of the permanganate ion corresponds with the region of maximum transmission of a signal green glass. Manufacturers recommend a specific glass for a given determination. Where the measurement justifies its use, a monochromatic illuminant, such as a particular line of the mercury arc, may be used.

The actual quantity measured depends upon the instrument. Some are designed to give directly the percentage of incident light transmitted; others have arbitrary scales or are read in terms of some units which must be converted to the amount of the desired constituent. Generally a curve is constructed, from a series of standard solutions, which coordinates concentration of the desired constituent and the corresponding read-

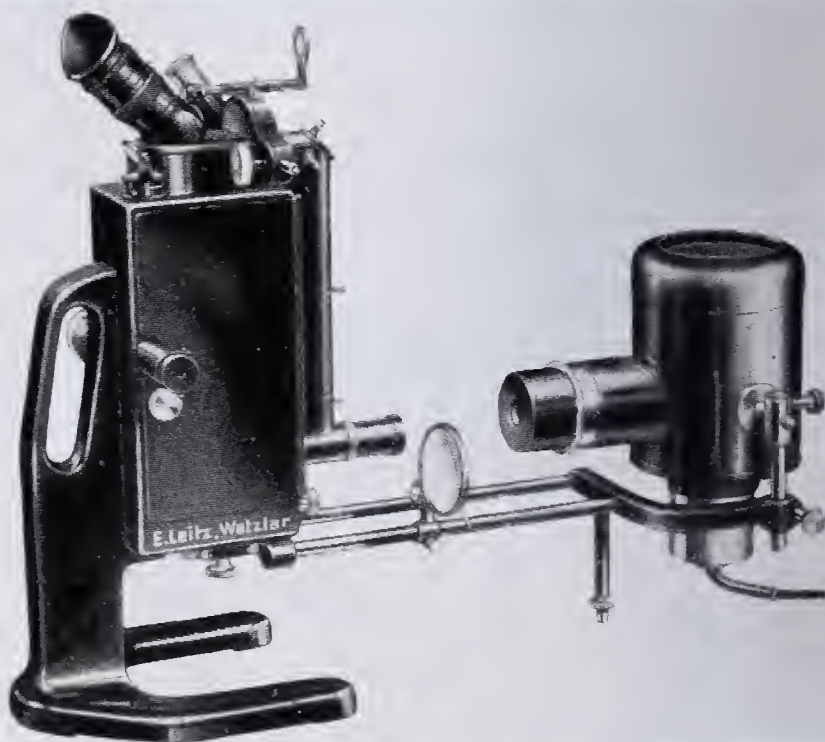


FIGURE 3. LEIFO PHOTOMETER



ing of the instrument. If the solution obeys Beer's law, one may apply the Bouguer-Beer equation

$$c = \frac{\log I_0/I}{el}$$

in which  $c$  = concentration (in moles per liter),  $l$  = thickness of the solution (in cm.),  $I_0$  = intensity of the incident light,  $I$  = intensity of the transmitted light, and  $e$  = molecular extinction coefficient. On plotting the determined transmittancies for a series of solutions on a logarithmic axis against the corresponding concentrations on an equal division axis a straight line is obtained. Since a given cell thickness is used and the slope of the curve is unimportant (as long as suitable sensitivity is obtained), it is necessary only to determine the transmittancy for a known solution and draw a straight line through the determined point to 100 per cent at zero concentration. If the solution does not obey Beer's law, as many do not, a curve must be constructed for a series of different concentrations of the desired constituent. Once the curve is established in either case there is no further use for standards.

Neither filter photometers nor comparators yield a fundamental color specification, since they do not really measure color as such nor provide data for calculating color stimuli. These instruments come nearest, perhaps, to measuring relative brightness. For certain solutions Keane and Brice (24) have proposed determining a "color index" with their

instrument from the formula  $100 - 100 G/R$ ,  $G$  and  $R$  being the measured transmittancies of the solution for the respective filters.

Although some analytical writers have referred to filter photometers as spectrophotometers, such an instrument can be considered at best as nothing more than an abridged spectrophotometer. If there are eight filters, the transmittancy of the sample can be determined for each one. On account of the width of the spectral band passed by each filter, these eight points cannot establish a reliable spectral transmission curve for materials having steep absorption bands. The broken line in Figure 2 is drawn through the points obtained on such an instrument (data provided by the manufacturer of the instrument), the wave lengths being those given by the manufacturer as the medium wave length for the filter. The smooth curve gives the spectrophotometric data for the same sample for a band width of  $5\text{ m}\mu$ .

On account of the differences in their construction, it is convenient to consider visual and photoelectric photometers separately.

*Visual Type.* In the Pulfrich photometer (38), as manufactured by Carl Zeiss, Inc., two light beams enter the optical system, one passing through the solvent only and the other through the solution. The observer brings the two halves of the optical field to a match and determines the magnitude of the absorption from the readings on the micrometer drum heads. A series of eight glass filters provides for isolating spectral bands approximately 20 to 25  $\text{m}\mu$  wide. In recent years many papers have described the use of this instrument as a means of determining

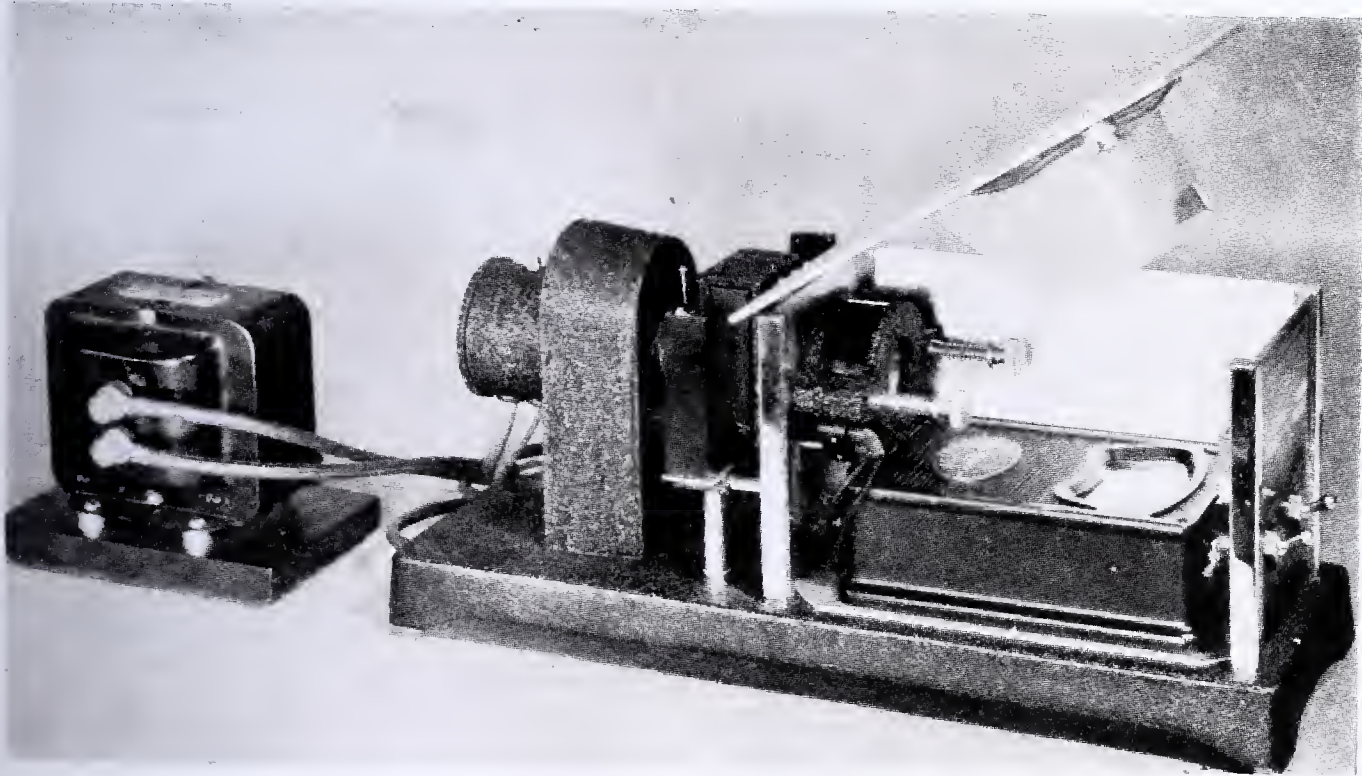


FIGURE 4. SHEARD AND SANFORD PHOTOMETER

- |                                 |                       |
|---------------------------------|-----------------------|
| T. Constant wattage transformer | F. Light filter       |
| S. Light source                 | P. Photoelectric cell |
| I. Iris diaphragm               | M. Microammeter       |
| L. Lens                         |                       |
| A. Absorption cell              |                       |



concentration of solutions, and for a variety of other optical purposes.

A more recent instrument of the same general type, illustrated in Figure 3, was introduced by E. Leitz, Inc., as the Leifo photometer (27). The relative intensity of the two light beams is varied by rotation of polarizing prisms, reading in extinction coefficients. Accompanying tables give the corresponding per cent transmittancy. The eight filters and a number of attachments provide for many optical measurements.

A third example is the neutral wedge photometer devised by Clifford (3). A calibration curve is constructed for a given determination by noting the position of the movable wedge for a series of known solutions.

**Photoelectric Type.** Probably the most notable changes in colorimetric instruments used by analysts followed the introduction of photoelectric cells. Both barrier-layer and photoemission types of cells are employed. Their use in filter photometers led the National Bureau of Standards to issue an extensive circular (12) which presents a critical evaluation of such devices.

Many variations are found in the electrical and optical details of the schemes which have been suggested. A few of these differences are noted in connection with specific examples cited below. While the general tendency has been to use arbitrary scales, a few instruments are designed to read transmittancy or amount of desired constituent directly. They are usually classified on the basis of the number of photocells used.

**One-Cell Instruments.** When only one photocell is used, the essential parts of the arrangement consist of a light source, a container for the sample, a photocell to receive the transmitted light, and some means of measuring the response of the photocell. In Figure 4 both the general appearance and the schematic arrangement of parts are shown for Sheard and Sanford's design (39), one of the earlier instruments. Similar devices are those of

Evelyn (8), the Fisher Scientific Co. (10), Müller (34), and Yoe and Crumpler (54).

In order to ensure constancy in the illuminant, and consequently in the response of the photocell, the electric current for the illuminant is provided by a storage battery or a constant power transformer. The response of the photocell is detected by means of a sensitive galvanometer or a microammeter. While it is generally necessary to calibrate the instrument for a given determination by correlating concentration of the desired constituent with microammeter or galvanometer readings, a direct reading scale may be incorporated. In Kudor's design (26) a different direct-reading scale can be turned into place for each of a number of constituents to be determined.

Evelyn's arrangement provides for the use of test tubes for the solution instead of the usual optically plane cells. It may also be used for samples of a micro size.

The absorption cell is used in different ways. If an arbitrary calibration curve is constructed, only one cell is needed and it may have any usable dimensions as long as it is always used in the same way for both known and unknown solutions. When the transmittancy is desired, preferably the cells should have optically plane faces and a definite thickness. Either the solvent and solution are measured successively in the same cell, or two optically interchangeable cells may be employed, one for the solution and one for the solvent.

**Two-Cell Instruments.** In order to avoid the provisions necessary to ensure constancy of operating current for the light source in one-cell instruments, investigators rather early proposed two-cell arrangements based on the idea that fluctuations would affect the two cells equally and thus be compensated.

One type of arrangement for two photocells is illustrated in Figure 5. The essential differences from one-cell arrangements are that two beams of light come from the illuminant, one going to each photocell, and that the response meter, in this case a galvanometer, is used as a null-point instrument. The ordinary alternating current line furnishes current for the illuminant.

The instruments described by Exton (9) and by Withrow Shrewsbury, and Kraybill (51) are examples of the use of two photoemission cells. The latter paper stresses particularly the electrical problems involved.

The use of barrier-layer cells has been more common, the apparatus of the American Instrument Co. (2), Keane and Bric (24), Lange (36), and Spekker (Hilger) (42) being representative examples of those currently advertised. The author has had good results with one adapted from the design of Wilcox (50) and equipped with Aklo filters to diminish the response lag in the photonic cells by absorbing the infrared radiation from the illuminant. In such instruments the two photocells may be used either in a series-opposing or a parallel connection. Bric (5) has reviewed various proposals for the circuits and given critical analysis of the arrangements and performance of one modification.

Certain modifications of this type of instrument make it possible to measure transmittancy directly by using two optically interchangeable absorption cells simultaneously, one containing the solvent only in one beam and one containing the solution in the other beam, as shown in Figure 5. Also, the absorption cell may be used in the same way as in one-cell instruments.

**SPECTROPHOTOMETERS.** Since the general role of spectrophotometry in colorimetry was presented in an earlier paper (30), reference should be made to it for information on visual and photoelectric types of instruments and their general analytical applications. The material presented here is limited to what seems necessary to relate spectrophotometers to the types of colorimetric instruments already discussed.

On account of their cost and the knowledge and experience required to keep them operating reliably, spectrophotometers are undoubtedly to be considered still as instruments primarily for research and standardization. They constitute, however, in the opinion of physicists, the most fundamental method of colorimetry available.

One uses a rather wide spectral band from the illuminant in filter photometers, the particular region depending upon the filter selected. In contrast to this, spectrophotometers have a single or double monochromator in which prismatic dispersion of light from the illuminant enables one to select any wave length desired. In addition, adjustment of the slits regulates the width of spectral band entering the photometer.

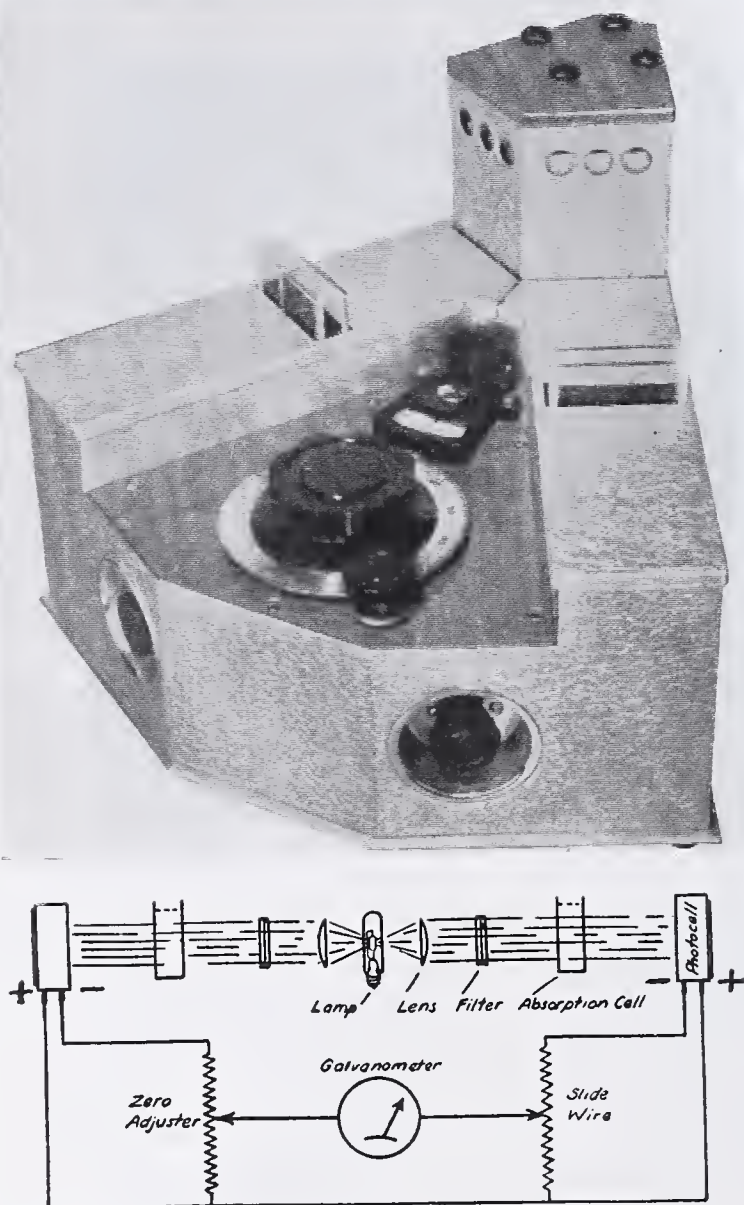


FIGURE 5. PHOTOMETER OF AMERICAN INSTRUMENT CO.



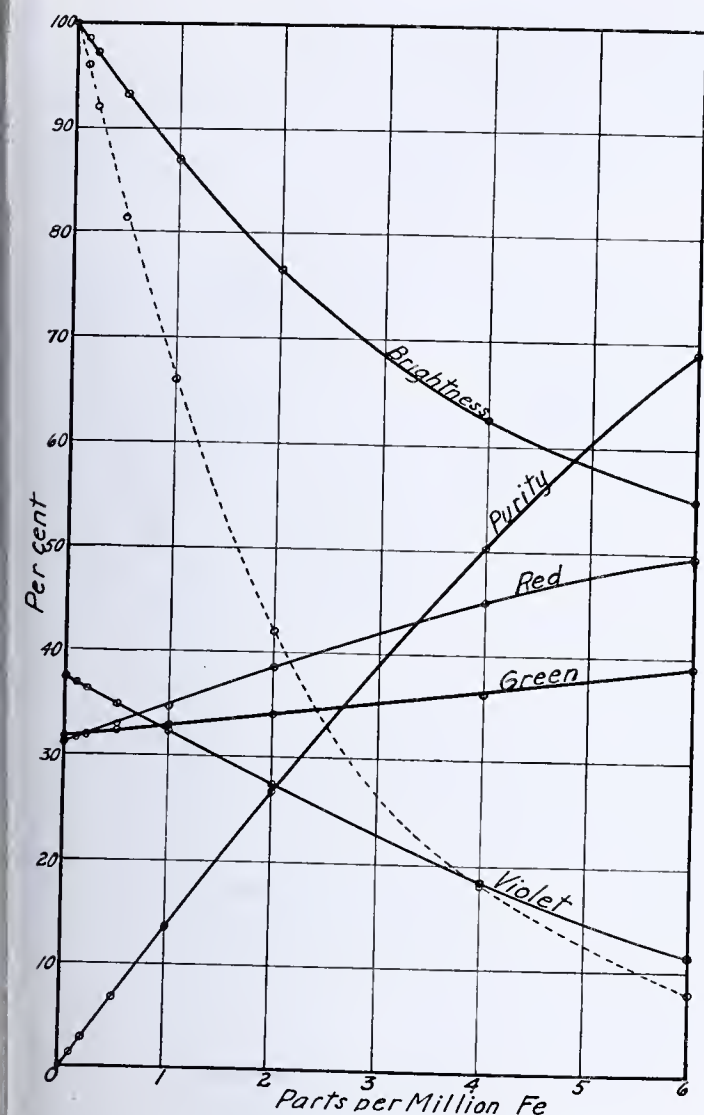


FIGURE 6. COLORIMETRIC VALUES FOR SOLUTIONS CONTAINING DIFFERENT AMOUNTS OF IRON

Broken curve is percentage transmittancy

Reference to Figure 2 shows the difference in the data obtained on a filter photometer and on a recording spectrophotometer set for a  $5\text{ m}\mu$  spectral band. Hogness, Zscheile, and Sidwell (21) used their photoelectric instrument with a band width of less than  $3\text{ \AA}$ . in the visible region.

The work of Mehlig (28) may be cited as representing colorimetric determinations made by means of a spectrophotometer. Whereas one usually thinks of colorimetric methods as applicable only to relatively small concentrations of material, his work included determinations in ores of as much as 21 per cent of copper and 57 per cent of iron.

Spectrophotometric curves provide the fundamental data for the calculation of numerical specifications of color for finite illumination and for an assumed normal observer. The data are expressed in tristimulus values as percentages of red, green, and violet, or in monochromatic terms as dominant wave length, in millimicrons, and as percentages of relative brilliance and colorimetric purity. Thus far analysts have made little use of such data. De Almeida (1) suggested determining pH values from a curve coordinating dominant wave length and pH for a given indicator. Using a recording spectrophotometer (33), Hardy's ten selected ordinates for calculation (19), and a recently described calculator (45), colorimetric specifications may be obtained fairly rapidly. Figure 6 illustrates how they may be correlated with concentration. The data shown are for solutions of iron treated with o-phenanthroline and were calculated for illuminant C from curves published recently (11). It is apparent that a

relatively high sensitivity may be obtained for this system by using the curves for relative brilliance or colorimetric purity. With less sensitivity any one of the tristimulus values could be used, green being the least sensitive of the three. It would seem possible, therefore, to use a stimulator in this way. The dominant wave length curve is too nearly horizontal to be of value. None of these curves gives the sensitivity of the transmittancy curve itself, which is shown as a broken line for the values at  $506\text{ m}\mu$ , the peak of the absorption band. Furthermore, the transmittancy does not necessitate any calculations.

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# The Use of Mercurous Chloride

## For the Separation, Detection, and Estimation of Easily Reduced Elements

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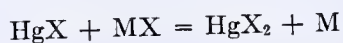
A GOOD many years ago during an attempt to prepare arsenic cyanide, it was observed that mercurous chloride would precipitate arsenic and a number of other easily reduced elements. Later these reactions were investigated in more detail and new methods were described (2, 3), adapting the reducing action of mercurous chloride specifically to the detection, estimation, and separation of minute quantities of gold, platinum, palladium, selenium, tellurium, and arsenic.

Although these reactions are simple and easy to observe, the previous literature on the subject had apparently been confined to an occasional statement in textbooks that soluble mercurous salts precipitate gold from solution. However, in 1927 Yasuda (4) reported that magnesium added to a strong acid solution of mercuric chloride would precipitate a cloud of finely divided metallic mercury, which would carry down as an amalgam any gold or silver in the solution. The precipitated amalgam was then fire-assayed to determine gold and silver. No significance was attached to the fact that the reduction of mercuric chloride with magnesium first produced a cloud of mercurous chloride, which in all probability was never completely reduced to metallic mercury. Yasuda used his method to determine the gold content of sea water near Japan and reported quantities of from  $\frac{1}{3}$  to 1 part per 100 million.

In 1935 Caldwell and McLeod (1) confirmed the effectiveness of Yasuda's procedure and among other things stated that as little as one part of gold in four billion parts of water could be quantitatively recovered. They called the precipitating agent a cloud of mercury mercurous chloride.

### General Characteristics of the Reaction

When mercurous salts are added to suitable solutions of gold, platinum, palladium, selenium, tellurium, and arsenic, these are reduced and precipitated as elements, the mercurous salts being oxidized to the mercuric. A general equation for the reaction is



This reaction is unidirectional under favorable conditions and proceeds rapidly even with highly insoluble mercurous salts such as the halides. These very insoluble mercurous halides not only rapidly throw the elements out of solution but quickly and completely adsorb them. These precipitated elements are colored, depending both upon the particular element and the amount present, and these colors afford the means for detection and estimation.

Powdered mercurous chloride is the most effective precipitating agent. It is highly insoluble and very reactive, and being heavy settles rapidly, carrying down the reduced and adsorbed elements. This makes separations easy. Mercurous chloride is also opaque and white and offers a good background for observing the colors of the adsorbed elements—for example, a very small amount of gold on mercurous

**The use of mercurous chloride for the detection, estimation, separation, and recovery of gold, silver, platinum, palladium, selenium, tellurium, arsenic, and iodine is described. Detections and estimations are made by colorimetric methods. Separations are made by using selective precipitating conditions.**

chloride may appear cream pink, purple, gray, or black, depending on the precipitating conditions.

Colored solutions do not interfere because they can be decanted from the precipitate. Precipitates are never colloidal or difficult to handle. The reaction is complete in a very short time. The manipulations are

simple and the equipment and reagents required are found in any laboratory.

In addition to their simplicity and extreme delicacy, these reactions are also unusually free from interference. The interfering substances are limited to those having strong oxidizing or reducing action. Nitrates, per salts, free halides, stannous chloride, and hypophosphites must not be present in appreciable quantities, but among this group only nitrates are likely to be encountered. Cupric and ferric salts, apparently because of their oxidizing action, may interfere present in sufficient quantity. Highly colloidal materials such as starch, dextrin, blood, or casein do not interfere, which suggests that these methods may have value for use with plant or body fluids.

TABLE I. PRECIPITATION WITH MERCUROUS CHLORIDE

Element Present	HCl Required for Precipitation in Cold	Boiling HCl Solution, 0.02% HgCl <sub>2</sub>	Preferred Conditions for Precipitations
Au	0 to concd.	0 to concd.	About 2% H <sub>2</sub> warm
Pt	0 to slight	0 to concd.	About 2% H <sub>2</sub> 0.02% HgCl <sub>2</sub> hot
Pd	0 to concd.	0 to concd.	About 2% H <sub>2</sub> warm
Se	6 to 15%, partial 16 to concd., complete	6 to 15%, partial 16 to concd., complete	About 20% H <sub>2</sub> cold
Te	6 to 15%, partial 16 to concd., complete	6 to 15%, partial 16 to concd., complete	About 20% H <sub>2</sub> cold
As (ous)	27% to concd.	27% to concd.	About 30% H <sub>2</sub> cold
I	0 to slight	None	Very slight acid, cold

Silver is precipitated quantitatively by mercurous chloride but this reaction has not been investigated in detail. Substantial quantities of silver on mercurous chloride produce cream color but small quantities are difficult or impossible to detect. The metals ruthenium, rhodium, iridium, and osmium usually occurring with platinum and palladium are not precipitated by mercurous chloride.

This study of the reducing action of mercurous chloride has been principally confined to very dilute solutions of easily reduced elements.

### Specific Characteristics of the Reaction

Mercurous chloride may or may not react with solutions of these easily reduced elements, depending upon conditions of acidity and temperature or the presence of interfering chemicals, and among these conditions a number have been found which are selective or specific with regard to one or more elements. This has permitted working out a scheme for separations as well as the determination of one element in the presence of others. Among the elements precipitated



by mercurous chloride, gold, platinum, and palladium are frequently found together as are selenium, tellurium, and arsenic; in fact, all six of these elements may occur together, so that any comprehensive scheme of analysis involving mercurous chloride required that conditions be found permitting selectivity and eliminating the possibility of one element interfering with another.

Table I shows some of the conditions which affect the mercurous chloride precipitation.

The second column shows the acid required for precipitation from cold solutions. Gold comes down in a neutral or concentrated acid solution. Platinum comes down in a neutral solution, but not when the acidity is more than slight. Palladium comes down in a neutral or concentrated acid solution. Selenium does not come down at all under 6 per cent, incompletely from 6 to 15 per cent, but completely from 16 per cent to concentrated. Tellurium reacts like selenium. Arsenic, which must be in the trivalent form, requires an acidity greater than 27 per cent. The iodine reaction is not a reduction as with the other elements, but a transposition, mercurous chloride becoming mercurous iodide and therefore highly colored. In very dilute solutions iodides do not transpose when the acidity is more than slight.

The third column of Table I shows the reactions in boiling acid solutions to which 0.02 per cent of mercuric chloride has been added. The mercuric chloride is added to prevent the mercurous chloride from decomposing with heat and turning gray or black which, of course, would mask any other color coming from the precipitated elements. Gold comes down from neutral or concentrated acid as in a cold solution. Platinum comes down with any acid concentration, whereas in a cold solution there is no reaction with acidity greater than slight. Palladium, selenium, tellurium, and arsenic precipitate with heat very much the same as without. Iodides in very dilute concentrations do not transpose at all, apparently owing to the effect of mercuric chloride rather than heat.

By simply changing the acidity, a variety of separations is possible. With a neutral solution the first three elements come down while the others do not. With cold 16 per cent acid only arsenic, platinum, and iodides remain in solution; with 30 per cent acid only platinum and iodides remain in solution; with boiling the platinum is precipitated, etc.

TABLE II. OUTLINE OF SEPARATIONS

	2% HCl solution of Au, Pd, Pt, Se, Te, and As Add 1% oxalic acid, boil to precipitate Au, filter
Au precipitate	Solution of Pd, Te, Se, Te, and As Cool, add HgCl to precipitate Pd, filter
Pd, HgCl precipitate	Solution of Pt, Se, Te, and As Add 0.02% HgCl <sub>2</sub> , add HgCl, boil, precipitate Pt, filter
Pt, HgCl precipitate	Solution of Se, Te, and As Add HCl to 20%, cool, add 5% NaHSO <sub>3</sub> , stand, boil, precipitate Se, filter
Se precipitate	Solution of Te and As Cool, add HgCl, precipitate Te, filter
Te, HgCl precipitate	Solution of As Add HCl to 28%. Add HgCl, precipitate As

In the last column the precipitating conditions usually employed for separations or estimations are given. For gold, 2 per cent acid solution is used. Gold comes down completely and rapidly in the cold but the color is usually gray, resembling platinum or palladium. On warming the precipitate on a water bath for a minute or two a characteristic purple or pink will develop.

For platinum a 2 per cent acid solution is used to which 0.02 per cent of mercuric chloride has been added. After adding the mercurous chloride, the mixture is heated on a boiling water bath for about 15 minutes, followed by a gentle boiling for about one minute which is usually sufficient for complete precipitation of platinum.

Palladium will precipitate readily in the cold when a 2 per cent acid solution is used, but some heat will intensify the coloring slightly.

With both selenium and tellurium a 20 per cent hydrochloric acid solution is used, without heat. The colors from these elements fade with heat or on standing several hours at room temperature. A 30 per cent acid solution is suitable for arsenic, without heat. If arsenic is in the (ic) form it should be reduced, sulfurous acid or sulfites being suitable. The color from arsenic also fades slowly with heat or long standing at room temperature. The iodide transposition will take place when the solution is slightly acid to litmus and cold.

Table II shows an outline of some separations made with the help of mercurous chloride.

Starting with a 2 per cent hydrochloric acid solution of gold, palladium, platinum, selenium, tellurium, and arsenic, add 1 per cent oxalic acid, boil to precipitate gold, and filter. Dissolve the precipitated gold with chlorinated acid, boil to remove chlorine, and precipitate with mercurous chloride for identification or estimation. The solution, which now contains palladium, platinum, selenium, tellurium, and arsenic, should be cooled to room temperature and palladium precipitated with mercurous chloride. Filter. The precipitate is a mixture of mercurous chloride and palladium, and the solution contains platinum, selenium, tellurium, and arsenic. Add 0.02 per cent of mercuric chloride followed by mercurous chloride and boil to precipitate platinum. The precipitate is a mixture of mercurous chloride and platinum.

If desired, mixtures of mercurous chloride with palladium, gold, or platinum can be separated by subliming the mercurous chloride. Make up the solution, which now contains selenium, tellurium, and arsenic, to 20 per cent hydrochloric acid and cool. Add 5 per cent of sodium acid sulfite, let stand for 15 minutes, boil to precipitate selenium, and filter. The precipitate is selenium alone which can be dissolved with chlorinated acid and reprecipitated with mercurous chloride. Cool the solution containing tellurium and arsenic, precipitate the tellurium with mercurous chloride, and filter. The precipitate is a mixture of tellurium and mercurous chloride and the solution contains arsenic which is precipitated with mercurous chloride after the acidity is brought up to 28 per cent.

General Method for Detections and Estimations

Detections are based on various colors, and estimations are based on the shades of such colors produced by the precipitated element. The shades produced by one element on a fixed amount of mercurous chloride depend principally upon the amount precipitated but also to a minor extent upon the solution concentration of the element before precipitation. Color variations may also be caused by temperature and solution purity; however, these possible sources of error are reduced to a minimum when standard controls are carried along under the same conditions as the test sample. It is usually desirable to extract a portion of the test sample with mercurous chloride and use this portion as a base for preparing a standard control. For each element there is a range over which the variation of color per unit of element is maximum. On either side of this sensitive range little change in color is produced by increased or decreased adsorption.

Hydrochloric acid is used to control the acidity of the solution; it should first be boiled with about 1 per cent of mercurous chloride, then permitted to stand for 48 hours, when the clear acid can be decanted for use. Sulfuric, hydrochloric, and possibly other nonoxidizing acids can be used.

In general the procedure for estimating has been to put 1 ml. or less of the test solution in a 100-ml. beaker, dilute to 5 ml. using hydrochloric acid or water as required, and then add 0.1 gram of mercurous chloride. With a little shaking the reaction is complete in a few minutes, after which the mercurous chloride is collected for observation by tilting the beaker.

Table III shows the colors developed on mercurous chloride by adsorption of the elements listed when 0.1 gram of mer-



TABLE III. COLORS ON MERCUROUS CHLORIDE

(Using 0.1 gram of HgCl and 5 ml. of solution)				
Element	0.1 Mg. <sup>a</sup>	0.01 Mg. <sup>a</sup>	0.001 Mg. <sup>a</sup>	0.0001 Mg. <sup>a</sup>
Au	Purple	Purplish pink	Light pink	Faint pink
Pt	Dark gray	Light gray	Cream	Light cream
Pd	Gray-black	Light gray	Grayish cream	Light cream
Se	Salmon	Pinkish cream	Light cream	...
Te	Brownish yellow	Brownish cream	Light cream	...
As	Brown	Pinkish brown	Pink	Cream
I	Greenish yellow	Light yellow	...	...

<sup>a</sup> Element present in 5 ml. of test solution.

TABLE IV. ACCURACY OF METHOD

Element	Accuracy with Approximately 0.1 Mg. of Element	Minimum Visible on 0.1 Gram of HgCl
	%	Mg.
Au	± 3	0.00005
Pt	± 5	0.0001
Pd	± 3	0.00005
Se	± 5	0.0002
Te	± 10	0.0005
As	± 5	0.00005
I	± 5	0.003

curous chloride is used with 5 ml. of test solution. Gold shades off from purple to pink, platinum from dark gray to cream, palladium from gray-black to cream, selenium from salmon to cream, tellurium from brownish cream to cream, arsenic from brown to pink to cream, and iodide from greenish yellow to light yellow. In each case the maximum color change is from about 0.1 to 0.01 mg. and whenever possible a solution carrying about 0.1 mg. should be used for estimations. With the larger amount the percentage of error is less.

Table IV shows the per cent accuracy of the method when working with about 0.1 mg. of element. The figures are an average of tests made with reasonably pure solutions and seem to compare favorably with other colorimetric estimations. The third column shows the smallest amount of each element on 0.1 gram of mercurous chloride visible to the unaided eye.

Arsenic Tests

A number of basically different chemical methods have been developed for detecting and estimating minute quantities of arsenic. The March and Gutzeit methods reduce arsenic to arsene, but require special apparatus and an experienced operator to give the best results. A strychnine or cocaine molybdate reagent has been proposed which gives a measurable turbidity with arsenic. Methods employing stannous chloride, sodium hypophosphite, or acid sodium thiosulfate have been used extensively to reduce solutions of arsenic, giving a brown color suitable for colorimetric estimations. These last methods require comparatively pure and colorless test solutions, and are somewhat lacking in accuracy and sensitivity. A method based on the formation of molybdenum blue from arsenomolybdate is probably among the most accurate and suitable for determinations over a rather broad range of arsenic content. Test solutions, however, should be colorless and a number of elements interfere. Finally, a novel test has recently been described,

depending on the odor given off by certain molds feeding on an arsenic solution.

Considering the possibilities of those methods just mentioned, it seems that the mercurous chloride method has certain outstanding advantages. Within a limited range its accuracy is equal to the best. The sensitivity apparently exceeds all others by a substantial margin. No apparatus is required and the manipulations are very simple. Interference is reduced to a negligible factor for many solutions; colored solutions do not interfere.

Additional Applications

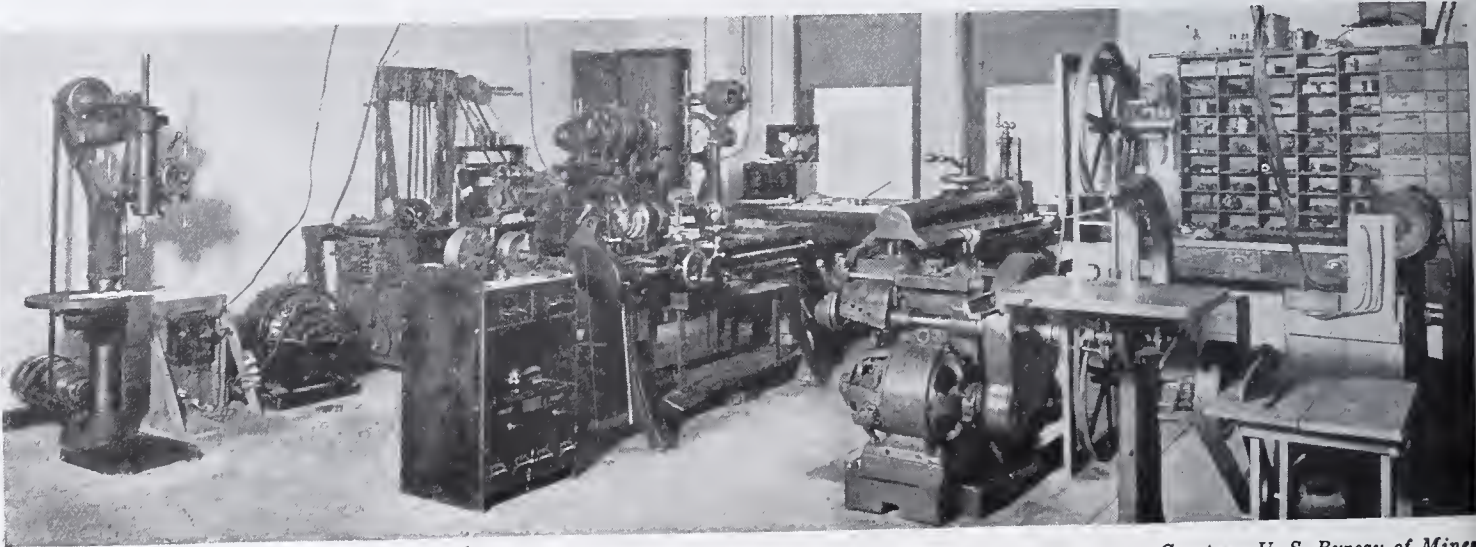
The use of mercurous chloride offers one of the most delicate colorimetric chemical tests known and its use for this purpose has been emphasized; however, mercurous chloride containing adsorbed gold, silver, platinum, or palladium may be fire-assayed without difficulty by methods such as those described by Caldwell and McLeod (1).

Mercurous chloride is also highly effective and economical in recovering gold, silver, platinum, and palladium from extremely dilute solutions. Commonly used precipitating agents do not offer simultaneous adsorption and for that reason precipitate these metals from dilute solutions as an extremely fine suspension, frequently colloidal and accordingly very difficult or impossible to recover.

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Courtesy, U. S. Bureau of Mines



# Determination of Halogens in Organic Compounds

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SINCE 1923 when Fajans and Hassel (6) applied adsorption indicators to the argentometric determination of inorganic halides, the use of these indicators for this purpose has become rather extensive (9, 10). In the field of organic analysis, however, they have been used successfully only for semimicroanalyses. Bobranski and Sucharda (2, 3) and later Hardy (7) using a 2- to 3-centigram sample for analysis burned it in an atmosphere of oxygen over a platinum catalyst. In the case of chlorides and bromides the combustion gases were passed over barium carbonate and the resulting barium halide was titrated with silver nitrate using eosin or fluorescein as adsorption indicator. For iodides, a 40 per cent solution of sodium sulfite was used as the absorption liquid, and the iodide formed after removal of excess sulfite by barium carbonate was titrated with silver nitrate using eosin as an indicator. Holscher (8) burned the sample in an air stream and passed the combustion gases through a 5 per cent hydrogen peroxide solution. After buffering with sodium acetate, he titrated the halide formed using dichlorofluorescein or eosin as adsorption indicator.

On a macroscale Bambach and Rider (1) found that dichlorofluorescein could be used successfully in the case of inorganic halides and organic hydrochlorides in alcohol-water solutions. They suggested the possibility of applying this titration in conjunction with the Stepanow method of reduction to the determination of the halogen content of organic substances.

In the work reported in this paper it was found that a combination of a modified Stepanow procedure and a subsequent titration with silver nitrate using adsorption indicators was a reliable and accurate method for determining the halogen content of a variety of organic halides.

## Experimental Procedure

The procedure employed for the reduction of the organic halides was based upon the modification of the Stepanow method proposed by Cook and Cook (4). The amounts of sodium and alcohol employed were calculated from the empirical rules of Drogin and Rosanoff (5), except for halogenated nitro compounds where the 150 per cent increase recommended by Cook and Cook was used.

A weighed sample of thoroughly desiccated organic halide (equivalent to approximately 25 cc. of 0.1 *N* silver nitrate, except in cases of halogenated nitro compounds where an amount approximately equivalent to 10 cc. of silver nitrate was used in order to avoid too great dilution of the solution to be titrated) was placed in a 250-cc. Erlenmeyer flask fitted with a reflux condenser, the constricted tip of which had been removed. In the case of solids the samples were weighed into small vials which were dropped into the Erlenmeyer flask. For the analysis of liquids, small vials were made by heating 6-mm. glass tubing until one end was sealed and pressing this end against a flat surface while soft. This tubing was then cut off at a length of 3 cm., resulting in a small vial which stood erect on the balance pan. During weighings the open end of the tube was closed by a small cork stopper. In transferring to the Erlenmeyer flask the cork was removed and the vial plus the liquid was dropped into the alcohol which was placed in the flask prior to the addition of the sample.

The reductions proceeded just as effectively in the Erlenmeyer flask as in the Kjeldahl flask recommended by Cook and Cook, while the titrations in the former were carried out much more easily than in the latter where the long neck interfered with the fall of drops from the buret to the flask.

The required amount of absolute alcohol previously distilled over metallic sodium in order to remove aldehydes was then added and the flask warmed over a low Bunsen flame until the sample had dissolved. Absolute alcohol free from aldehyde was found necessary for the success of the determination since otherwise, after reduction, the liquid was found to be colored so darkly, owing to polymerization of the aldehyde in the alkaline medium, that the final titration could not be performed. The burner was then removed and the required amount of sodium (Baker's c. p. grade) cut into rods about 2.5 cm. long was introduced through the top of the condenser. At least 0.5 hour was allowed for the dissolution of the sodium and at no time were there more than three pieces of sodium in the flask. During the latter part of the addition, the reaction of the sodium was aided by a small flame under the flask. The solution was then gently refluxed for one hour, after which it was allowed to cool and diluted with about 15 cc. of water, at first drop by drop and then by larger amounts as the violence of the reaction subsided. The flask was now held under running water, and two drops of phenolphthalein were added, followed by addition of approximately 6 *N* nitric acid drop by drop until the solution was decolorized. The required amount of adsorption indicator was next added (8 drops of dichlorofluorescein in the case of chlorides and 2 drops of eosin for bromides and iodides) and the solution was titrated with standard 0.1 *N* silver nitrate until the color changes described below occurred.

As the silver nitrate was added the silver halide first precipitated in colloidal form. As more reagent was added the precipitate coagulated and settled to the bottom of the flask in the form of flocs. Just before reaching the end point the flocs formed a large number of grainy particles which in the case of dichlorofluorescein became distinctly pink and in the case of eosin changed from a pale pink coloration to a bright rose red at the equivalence point. These color changes were best observed by keeping the contents of the flask in motion during the titration.

## Experimental Results

The results of analyses of a variety of halogenated organic compounds using the above described procedure appear in Table I.

TABLE I HALOGEN CONTENT OF COMPOUNDS ANALYZED

Compound	Determinations	Theoretical Halogen %	Halogen Found %	Average Deviation P. p. m.
Chloroacetamide	5	37.91	38.06	4.7
Chlorobenzene	5	31.52	31.49	5.1
<i>p</i> -Dichlorobenzene	5	48.26	48.35	2.7
<i>m</i> -Nitrochlorobenzene	3	22.52	22.20	3.2
Hexachlorobenzene <sup>a</sup>	4	74.74	74.71	0.3
Hexachloroethane	4	89.84	89.45	1.7
Bromobenzene	5	50.92	50.81	0.8
<i>p</i> -Dibromobenzene	5	67.77	67.67	1.6
<i>m</i> -Nitrobromobenzene	4	39.57	39.60	2.5
<i>p</i> -Nitrobromobenzene	4	39.57	39.63	1.5
1,3,5-Tribromobenzene	4	76.19	76.13	1.6
2,4,6-Tribromoaniline	4	72.71	72.48	1.3
Dibromocinnamic acid	5	51.88	51.99	2.3
3-Bromocamphor	5	34.59	34.69	3.2
Iodoform	5	96.70	96.50	2.4

<sup>a</sup> The reduction of hexachlorobenzene because of difficult solubility required quantities of alcohol and sodium 25% in excess of that calculated from the empirical rules.

Dichlorofluorescein was used as the indicator for chlorine determinations and eosin for bromine and iodine. Attempts to use dichlorofluorescein for bromine determinations led to unsatisfactory results. The precipitate darkened so quickly that the detection of the equivalence point during the titration became very difficult or impossible. These results differ from those secured by other investigators (8) in the determination of the halogen content of inorganic halides where it was found that dichlorofluorescein could be used for all three.



In the case of the iodine determination it was found that 6 *N* nitric acid could be employed for the acidification prior to titration instead of the very dilute acid used by earlier investigators. The addition was made very slowly while the flask was cooled in a bath of ice and water. Five determinations of the iodine content of iodoform showed no appreciable oxidation of the iodide.

### Summary

The halide content of a variety of halogenated organic compounds can be determined satisfactorily by a modified Stepanow method of reduction, followed by titration with silver nitrate using dichlorofluorescein for chlorine and eosin for bromine and iodine as adsorption indicators.

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# Calcium Oxalate Monohydrate as a Weighing Form for Calcium

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PROBABLY the most accurate weighing form for calcium after precipitation as the oxalate is the carbonate (8), but the close control of temperature required in the method of Willard and Boldyreff makes the method unavailable to analysts who do not have the necessary equipment. Although good results can be obtained by weighing calcium as the oxide, special precautions must be taken to prevent the absorption of moisture, and the low molecular weight is a disadvantage. Calcium sulfate is not a convenient weighing form and is used only infrequently.

Calcium oxalate monohydrate would possess distinct advantages as a weighing form if the accuracy were sufficiently high. The possible sources of error involved include retention of foreign water (adsorbed and/or included) after drying, loss of hydrate water on drying, and coprecipitation of ammonium salts or oxalic acid. The ideal procedure from the standpoint of simplicity would involve drying the washed precipitate at room temperature after treatment with alcohol and ether or with acetone. Goy (3), who first proposed calcium oxalate monohydrate as a weighing form, dried the precipitate at 100° to 105° C. Dick (1), on the other hand, washed the precipitate with alcohol and ether, placed the crucible for a short time in a vacuum desiccator, and then weighed. Others (7) have used the same or a similar procedure. Moser and von Zombory (5) raised objections to the method of Dick, and according to them the results obtained by this procedure are much too high (1.6 to 3 per cent). Haslam (4) also obtained high results by Dick's method and by drying at 100° C. The monohydrate does not appear to be in good repute as a weighing form for calcium in macroanalysis, at least not in America, but it is frequently used in microanalysis. Since the statements in the literature regarding the use of the monohydrate as a weighing form are contradictory, the authors have precipitated calcium oxalate under various conditions and tested the suitability of this method of weighing calcium.

### Experimental

In most of the determinations the amount of calcium taken was obtained from the weight of calcium carbonate of known

calcium content. Two preparations of calcium carbonate were used:

PRODUCT I. This product was prepared by adding 0.05 *M* calcium chloride solution to excess hot 0.05 *M* ammonium carbonate solution, washing the precipitate with hot water, and drying at 150° C. The preparation contained only a trace of chloride and magnesium was not detectable. The calcium carbonate content of the product was determined acidimetrically by adding a slight excess of hydrochloric acid and back-titrating with sodium hydroxide. The hydrochloric acid was standardized gravimetrically by determining the chloride as silver chloride. Weight burets were used throughout. Three determinations yielded the values 99.885, 99.87, and 99.84 per cent of calcium carbonate or an average of 99.87 per cent. Known amounts of this product were weighed out, dissolved in hydrochloric acid, and used in most of the determinations of Table I. In a few cases a calcium chloride solution was used which had been standardized by evaporating a suitable volume to dryness and converting the residue to calcium sulfate.

PRODUCT II. This product, which had been prepared by J. J. Lingane of this laboratory for use in the J. Lawrence Smith method of decomposition for the alkali determination, was obtained by dissolving c. p. calcium carbonate in hydrochloric acid, precipitating with ammonia and ammonium carbonate in hot solution, and drying the washed precipitate at 130° C. Gravimetric determination of calcium in the product (calcium carbonate as weighing form), with a correction for solubility loss of calcium oxalate, yielded the value 98.87 per cent of calcium carbonate. The calcium carbonate content was also determined acidimetrically by using hydrochloric acid which had been standardized against potassium bicarbonate specially prepared as a primary standard. Three titrations with weight burets gave 98.89, 98.91, and 98.91 per cent of calcium carbonate. The value 98.90 per cent has been used in calculating the amount of calcium from the weight of calcium carbonate taken. Product II was used in all the determinations of Table II.

The precipitations were made as indicated in the tables. Porous porcelain and sintered-glass crucibles were used to collect the precipitates, and 50 to 75 ml. of cold water were used for washing.

Tables I and II give some of the results obtained in investigating the suitability of calcium oxalate monohydrate as a weighing form. A number of the results in Table I were obtained in an earlier study (6) of the water content of calcium oxalate in which precipitation was made in neutral



TABLE I.  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  AS A WEIGHING FORM FOR CALCIUM

Conditions of Precipitation	(Precipitated by ordinary methods)					
	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ Taken Gram	Temperature of Drying ° C.	Time of Drying Hours	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ Found Gram	Error	
					Mg.	%
50 ml. of 2.0% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ added slowly to 200 ml. of hot neutral calcium chloride solution. Filtered after cooling to room temperature	0.4458	25 (R. H. <sup>a</sup> = 57%)	120	0.4495	+3.7	+0.83
		100-105	5	0.4470	+1.2	+0.27
		100-105	15	0.4462	+0.4	+0.09
		100-105	15	0.4463	+0.5	+0.11
		105-110	46	0.4459	+0.1	+0.02
		110-115	18	0.4451	-0.7	-0.16
		115-120	22	0.4433	-2.5	-0.56
50 ml. of 2.0% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ added slowly to 200 ml. of hot calcium solution containing 1 drop of 2 N ammonium hydroxide and 2 grams of $\text{NH}_4\text{Cl}$	0.3758	115-120	20	0.412	-34	-7.6
		105	23	0.3782	+2.4	+0.64
		105	25	0.3780	+2.2	+0.59
		110	69	0.3790	+3.2	+0.85
		115-120	45	0.3665	-9.3	-2.5
As in (2) except 20 ml. of 2.5 N ammonia and 2 grams of $\text{NH}_4\text{Cl}$ present	0.4518	115-120	5	0.4363	15.5	-3.4
		115-120	2	0.4346	17.2	-3.8
		115-120	3	0.4320	19.8	-4.4
		110	15	0.4112	40.6	-9.0
50 ml. of 2.0% $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ added to 200 ml. of hot calcium solution containing 1 ml. of concentrated hydrochloric acid; solution then neutralized with 1 N ammonia and 0.5 ml. added in excess. Filtered when cold	0.4501	115-120	1	0.4523	+2.2	+0.49
		115-120	2	0.4516	+1.5	+0.33
		115-120	17	0.4519	+1.8	+0.40
As in (4) except 50 ml. of 2.0% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ used	0.3641	25	24	0.3678	+3.7	+1.01
		25 (R. H. = 57%)	24	0.3680	+3.9	+1.07
		25 (R. H. = 0%)	6 weeks	0.3672	+3.1	+0.85
		105	1	0.3673	+3.2	+0.87
		115	2	0.3672	+3.1	+0.85
50 ml. of 2.0% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ added to 175 ml. of hot calcium solution containing 2 ml. of concentrated hydrochloric acid; neutralized with 6 N ammonia added rapidly dropwise. Filtered after two days	0.7221	25	...	0.7249	+2.8	+0.39
		107	2	0.7206	-1.5	-0.21
		110	2	0.7195	-2.6	-0.36
		25	1	0.7225	+0.4	+0.06
		105	18	0.7217	-0.4	-0.06
		105	2	0.7213	-0.8	-0.11
		105	2	0.7213	-0.8	-0.11
As in (6) except 1 ml. of concentrated hydrochloric acid. Filtered after 4 hours	0.7219	25	...	0.7273	+5.4	+0.75
		105	5	0.7219	0.0	0.00
		105	1	0.7221	+0.2	+0.03
		105	40	0.7222	+0.3	+0.04
25 ml. of 4% $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ added to 100 ml. of cold calcium solution containing 1 ml. of 4 N acetic acid. Digested at 90° for 20 hours, cooled, filtered, and precipitate finally washed with alcohol and ether	0.3648	25	...	0.3652	+0.4	+0.11
		105	20	0.3649	+0.1	+0.03
		25 (R. H. = 29%)	24	0.3650	+0.2	+0.05
As in (8)	0.3648	25	...	0.3657	+0.9	+0.25
		105	18	0.3654	+0.6	+0.16
		110	0.5	0.3653	+0.5	+0.14
		25 (R. H. = 29%)	24	0.3656	+0.8	+0.22

<sup>a</sup> Relative humidity.

acid, and ammoniacal medium. Table II contains the results obtained by applying the precipitation method of Willard and Chan (9) in which the strongly acid solution of calcium containing an excess of oxalate is heated with urea; the ammonia produced by the hydrolysis of the urea slowly neutralizes the acid and a very coarse precipitate of calcium oxalate is thus formed. In the column headed "temperature of drying," 25 indicates that the precipitate was dried at room temperature by drawing air through the crucible for 5 to 10 minutes after washing with alcohol and ether (Table I) or acetone (Table II). In some cases the precipitate was dried further over concentrated sulfuric acid and this is indicated by R. H. (relative humidity) = 0 per cent. In other cases the precipitate was placed in a hygrostat of saturated sodium bromide, calcium chloride, or potassium chloride solution, respectively, and the corresponding relative humidity is then indicated. The same precipitate was used throughout each numbered experiment and was dried under various conditions and time in the order shown. In some of the experiments of Table II the precipitate was finally ignited to calcium carbonate according to the directions of Willard and Boldyreff (3), and in a few cases the precipitate was titrated with potassium permanganate (using weight burets) by the method of Fowler and Bright (2), the permanganate being standardized against Bureau of Standards sodium oxalate dried at 105° C. The permanganate titrations were made by Donald Smith.

### Discussion of Results

Calcium oxalate monohydrate precipitated in the usual way (Table I, Nos. 1 to 7) from neutral, ammoniacal, or acid medium retains foreign water after air-drying at room temperature, the amount ranging from about 0.3 to 1 per cent

or more. The customary method of precipitation from hydrochloric acid solution, with final neutralization by ammonium hydroxide, gives decidedly high results (variable but averaging about 0.75 per cent). The foreign water is not removed by keeping the precipitate over concentrated sulfuric acid. Although drying the precipitate at 105° C. or above gives better results, the method is not to be recommended unreservedly, because the dried monohydrate may still contain foreign water; in some cases the amount is very small. The results of drying at 105° C. are variable, the amount of foreign water retained apparently depending upon the relative humidity of the atmosphere. Another objection to drying at 105° C. or above is the possibility of loss of hydrate water. At 100° to 105° C. the monohydrate does not decompose easily under the conditions of humidity usually obtaining, but one cannot be certain that the product weighed is actually the monohydrate. At 110° to 120° C. the monohydrate can easily lose essential water in a dry atmosphere.

If calcium oxalate is precipitated in cold solution in the presence of acetic acid (to prevent the formation of basic oxalate) by the sudden addition of ammonium oxalate, and the mixture is then digested for 20 hours near the boiling point, the product is but slightly hygroscopic and contains relatively little occluded water after air-drying (Nos. 8 and 9, Table I). Precipitation under these conditions gives a precipitate containing a high proportion of the di- and trihydrates of calcium oxalate which are unstable in hot solution. Accordingly on digestion the precipitate recrystallizes and relatively "perfect" crystals of monohydrate are obtained which retain only small amounts of foreign water (6). However, the method suffers from the practical disadvantage that the small size of the final crystals tends to make filtration slow.



A second and better method of obtaining a precipitate of calcium oxalate monohydrate containing but a small amount of foreign water consists in precipitation by the method of Willard and Chan (9). From the results of determinations 1, 2, and 3 in Table II it will be seen that the neutralization

of the acid solution by the hydrolysis of urea must not take place too rapidly. When 10 or 15 grams of urea are used in 200 ml. of solution containing 5 ml. of concentrated hydrochloric acid and the neutralization is completed in 1 to 2 hours, the results are high to the extent of 0.2 to 0.5 per cent

TABLE II.  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  AS A WEIGHING FORM FOR CALCIUM  
(Precipitated by method of Willard and Chan)

No.	Conditions of Precipitation	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ Taken Gram	Temperature of Drying ° C.	Time Hours	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ Found Gram	Error Mg.	Error %	$\text{CaCO}_3$ Found Gram	Error Mg.	Error %
1	1.0 gram of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and 10 grams of urea added to 200 ml. of Ca solution containing 5 ml. concentrated hydrochloric acid. Heated near boiling point for 2 hrs. Allowed to cool 30 min. before filtration	0.6796	25 25 (R. H. = 85%) 105 105 25 (R. H. = 85%) 25 (R. H. = 85%) 120 25 (R. H. = 85%) 25 (R. H. = 85%) 25 (R. H. = 85%) 25 (R. H. = 85%)	... 18 5 40 23 48 24 48 48 48 24	0.6809 0.6808 0.6799 0.6792 0.6797 0.6798 0.625 0.6766 0.6790 0.6798 0.6798	+1.3 +1.2 +0.3 -0.4 +0.1 +0.2 -5.5 -3.0 -0.6 +0.2 +0.2	+0.19 +0.18 +0.04 -0.06 +0.01 +0.03 -8.1 -0.44 -0.09 +0.03 +0.03			
2	As in (1) except neutralization completed in 1.25 hrs. Cooled to room temperature before filtration	0.3617	25 25a 105 105	20 2 48	0.3633 0.3630 0.3622 0.3618	+1.6 +1.3 +0.5 +0.1	+0.44 +0.36 +0.14 +0.03	0.2476	-0.2	-0.08
3	As in (1) except 15 grams of urea. Neutralization completed in 1.25 hrs. Cooled to room temperature before filtration	0.7217	25 105 105 105 105 105 105 120	1 1 22 20 2 20 4	0.7255 0.7244 0.7240 0.7224 0.7180 0.7200 0.7216 0.702	+3.8 +2.7 +2.3 +0.7 -3.7 -1.7 -0.1 -20	+0.53 +0.37 +0.32 +0.10 -0.51 -0.24 -0.01 -2.8	0.4943	-0.1	-0.02
4	1.0 gram of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and 5 grams of urea added to 200 ml. of Ca solution containing 5 ml. of concentrated hydrochloric acid. Digested overnight at 80°-90°. Cooled to room temperature before filtration	0.7220	25 105 105	1 2.5	0.7223 0.7218 0.7214	+0.3 -0.2 -0.6	+0.04 -0.03 -0.08	0.4944	-0.2	-0.04
5	As in (4)	0.6139	25 25 (R. H. = 85%)	48	0.6137 0.6135	-0.2 -0.4	-0.03 -0.07			+0.03 <sup>b</sup>
6	As in (4)	0.3615	25 105 105 105	1 1 1	0.3621 0.3616 0.3615 0.3614	+0.6 +0.1 0.0 -0.1	+0.17 +0.03 0.00 -0.03	0.2474	-0.2	-0.08
7	As in (4)	0.3617	25 25 (R. H. = 85%) 105 25 (R. H. = 85%)	1.5 1 1	0.3622 0.3622 0.3618 0.3621	+0.5 +0.5 +0.1 +0.4	+0.14 +0.14 +0.03 +0.11	0.2475	-0.3	-0.12
8	As in (4)	0.1448	25 105	1	0.1457 0.1453	+0.9 +0.5	+0.62 +0.35	0.0992	0.0	0.0
9	As in (4)	0.1449	25 105	2.5	0.1449 0.1444	0.0 -0.5	0.0 -0.35			
10	As in (4)	0.1449	25 25 (R. H. = 85%) 105 25	20 1 24	0.1455 0.1456 0.1452 0.1456	+0.6 +0.7 +0.3 +0.7	+0.41 +0.48 +0.21 +0.48			+0.68 <sup>b</sup>
11	As in (4)	0.1499	25 25 (R. H. = 85%) 25 (R. H. = 85%)	48 170	0.1500 0.1498 0.1497	+0.1 -0.1 -0.2	+0.07 -0.07 -0.13			+0.16 <sup>b</sup>
12	As in (4)	0.1363	25 25 (R. H. = 85%) 120 25 (R. H. = 85%)	24 24 48	0.1368 0.1369 0.121 0.1369	+0.5 +0.6 ... +0.6	+0.37 +0.44 ... +0.44			+0.41 <sup>b</sup>
13	As in (4)	0.0722	25 105	2.5	0.0724 0.0719	+0.2 -0.3	+0.3 -0.4			
14	As in (4) except 0.30 gram of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	0.1705	25 25 (R. H. = 85%) 105	20 1	0.1710 0.1708 0.1703	+0.5 +0.3 -0.2	+0.29 +0.18 -0.12			
15	1.0 gram of ammonium oxalate and 5 grams of urea added to 200 ml. of Ca solution, acidified with 5 ml. of hydrochloric acid, containing 0.10 gram of sodium chloride. Digested 18 hrs. (80-90°)	0.3616	25 105 105	2 1	0.3631 0.3628 0.3628	+1.5 +1.2 +1.2	+0.41 +0.33 +0.33	0.2481	+0.4	+0.16
16	As in (15) except 0.03 gram of NaCl	0.3615	25 25 (R. H. = 57%) 105 105	1 3	0.3623 0.3624 0.3622 0.3619	+0.8 +0.9 +0.7 +0.4	+0.22 +0.25 +0.19 +0.11	0.2475	-0.1	-0.04
17	1.0 gram of ammonium oxalate and 5 grams of urea added to 200 ml. of Ca solution, acidified with 5 ml. of hydrochloric acid, containing 0.100 gram of $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Digested 24 hrs. at 80-90°. Filtered while still hot	0.3615	25 105 105	1 3	0.3616 0.3610 0.3610	+0.1 -0.5 -0.5	+0.03 -0.14 -0.14	0.2471	-0.5	-0.20
18	As in (17) except solution cooled to room temperature before filtration	0.3617	25 25 (R. H. = 85%) 105 105 25 (R. H. = 85%) 105	2 2 3 48 3	0.3621 0.3619 0.3612 0.3607 0.3616 0.3600	+0.4 +0.2 -0.5 -1.0 -0.1 -1.7	+0.11 +0.06 -0.14 -0.28 -0.03 -0.47	0.2478	0.0	0.00

<sup>a</sup> Over anhydrous calcium chloride.  
<sup>b</sup> From permanganate titration.



after air-drying. On the other hand, when 5 grams of urea are taken for 200 ml. of solution containing 5 ml. of concentrated hydrochloric acid and the hydrolysis is allowed to proceed overnight at 80° to 90° C. the error is reduced to +0.2 per cent or less for amounts of calcium equivalent to 0.25 to 0.5 gram of calcium carbonate. For smaller amounts of calcium (0.05 to 0.1 gram of calcium carbonate) under these conditions there is a distinct tendency for the positive error to increase, which is attributable mainly to coprecipitation of oxalic acid; in one case (No. 8) the error amounted to +0.6 per cent. The oxalate content of precipitates 10, 11, and 12 as determined by permanganate titration indicates that there is appreciable coprecipitation of ammonium oxalate, acid calcium oxalate, or oxalic acid with the smaller amounts of calcium oxalate, under the conditions of precipitation used. The larger amounts of precipitate (Nos. 1 and 5) show a normal oxalate content.

If the precipitate is dried at 105° C. the results are closer to the theoretical than when the precipitate is air-dried, but this method is not recommended because of the possibility of loss of hydrate water (see No. 3, Table II, in which some decomposition took place after long heating at 105° C.).

The coprecipitation of sodium is marked (Table II, No. 15) and only small amounts (No. 16) may be present unless a reprecipitation is made. Magnesium is not appreciably coprecipitated when present in small amounts, as shown by determinations 17 and 18 of Table II; these results indicate that even if a precipitate of calcium oxalate is badly contaminated by magnesium it can be freed from the latter element if the reprecipitation is made by the urea-hydrolysis method.

### Recommended Procedure

Prepare a solution of calcium salt containing the equivalent of 0.2 to 0.5 gram of calcium carbonate in 175 to 200 ml. of solution, add 5 ml. of concentrated hydrochloric acid, and heat nearly to the boiling point. Add 1.0 gram of ammonium oxalate monohydrate dissolved in approximately 20 ml. of hot water (no precipitate should form) and then 5.0 grams of reagent quality urea dissolved in a similar volume of cold water. After mixing, heat at 80° to 90° C. until the solution is distinctly basic to methyl orange (overnight). Cool the solution and collect the precipitate in a porous porcelain, sintered-glass, or Gooch crucible which has been weighed after standing 10 to 15 minutes in the air. Wash the precipitate with small portions of cold water and then with three or four 2-ml. portions of reagent quality acetone. Draw air through the crucible for 5 to 10 minutes and weigh. It is well to let the crucible stand on the balance pan for 10 to 15 minutes after the first weighing, and then to reweigh to be certain that the weight is constant.

In the presence of appreciable amounts of sodium or magnesium the first precipitation of calcium oxalate may be made by the ordinary method, and after washing with dilute ammonium oxalate solution the precipitate may be dissolved in hydrochloric acid and reprecipitated as described in the previous paragraph; in this case the amount of ammonium oxalate added in the final precipitation need not be more than 0.2 to 0.3 gram.

### Summary

Calcium oxalate monohydrate precipitated from neutral or ammoniacal solutions, or by neutralizing a hydrochloric acid solution with ammonia, retains foreign water after washing with acetone or alcohol and ether, and air-drying. Drying the precipitate at 105° C. and above yields results closer to the theoretical than does air-drying at room temperature, but this method of drying cannot be recommended without reservation because considerable amounts of water may still be retained, constant weight is not always easily attained, and the precipitate may lose monohydrate water in a dry atmosphere.

If calcium oxalate is precipitated slowly from an acid solution by gradual neutralization of the acid by the hydrolysis

of urea, it may be weighed as the monohydrate after washing with acetone. The solution, containing 5 ml. of concentrated hydrochloric acid per 200 ml., is treated with 5 grams of urea and digested at 80° to 90° C. until the acid has been neutralized. In this manner results accurate to approximately 0.2 per cent can be obtained with 0.2 to 0.5 gram of calcium carbonate; with amounts of calcium corresponding to 0.05 to 0.1 gram of calcium carbonate results tend to be high.

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## Glass Liner for High-Pressure Hydrogenation Bomb

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THE glass container shown in the accompanying figure has proved satisfactory as a liner for high-pressure hydrogenation bombs. It has been constructed in net capacities of 10 and 30 cc., and the design is feasible for larger volumes.

The body of the liner should fit the bomb snugly and, as shown, the joint should be rimless. A steel compression spring maintains closure and prevents rotation of the liner. Correct alignment of the gas inlet tube is assured by a mark on the rim of the male member of the joint which corresponds with the upper end of the constricted tube. A circular mark around the body of the tube about 5 mm. below the gas inlet serves as a reference point for calibration.

The authors have not succeeded in repairing broken liners which had been used at high temperatures and high pressures of hydrogen, owing to apparent absorption and retention of gas, which is liberated at glass-working temperatures causing the glass to froth.



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# Determination of Potassium with Hexanitrodiphenylamine (Dipicrylamine) Reagent

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**Gravimetric and volumetric procedures are given for the determination of macro- and microquantities of potassium as dipicrylamine; and a colorimetric procedure for the determination of microquantities (10 to 100 gamma).**

**H**EXANITRODIPHENYLAMINE or dipicrylamine is a relatively weak acid which is practically insoluble in water. Its potassium, ammonium, rubidium, and cesium salts are slightly soluble in water, have an orange-red to red color, and are crystalline. Poluektoff (7) was the first to use a solution of the sodium salt of dipicrylamine as a reagent for the detection of potassium. Van Nieuwenburg and van der Hoek (6) described the crystal habit of the above salts and recommended the reagent for the microchemical detection of potassium, even in the presence of cesium.

Sheintz (10) found that in addition to the above-named metals thallous thallium, beryllium, zirconium, lead, and mercuric mercury gave colored crystalline precipitates with the sodium salt of dipicrylamine; while aluminum, ferric iron, chromic chromium, nickel, cobalt, copper, bismuth, vanadium, titanium, thorium, and mercurous mercury gave amorphous precipitates. The reagent has an alkaline reaction and the last-mentioned group of cations should yield a precipitate which may consist of the hydrous oxide or some basic salt.

Feigl (3) includes the sodium salt of dipicrylamine in his review of spot tests for potassium. According to the authors' experience filter paper impregnated with the reagent is very suitable for the detection of potassium, even in the presence of much sodium and other cations.

Winkel and Maas (11) give procedures for the quantitative determination of potassium, either by weighing the precipitate or by conductometric titration of a solution of the precipitate in a mixture of acetone and water. Portnov and Afanas'ev (8) using the titration method report an accuracy of 0.5 to 1.5 per cent. Recently Kielland (5) has applied the reagent to the colorimetric determination of potassium in fertilizers by using a gradation photometer.

Using 10 mg. of potassium and following the directions of Winkel and Maas for gravimetric determination, the authors found that results were consistently about 3 per cent low. This prompted them to make a systematic study of the sources of error, which led to the development of satisfactorily accurate procedures for the determination of macro- and microquantities of potassium. The solubility of the potassium salt in water and in an excess of reagent is appreciable and varies strongly with the temperature. The solutions are decomposed by acid with a separation of the free amine. The potassium salt is freely soluble in acetone and also soluble in ether, ethanol, and methyl amyl ketone, but insoluble in chloroform, dichloroethane, carbon tetrachloride, and benzene. The free amine is very slightly soluble in water (light yellow color), insoluble in dilute mineral acids, chloroform, carbon tetrachloride, dichloroethane, and benzene, but soluble in acetone, ether, and methyl amyl ketone. Indications have been obtained that the potassium salt does not behave as an ideally strong electrolyte in water and in organic solvents.

The main source of error was found in the relatively great solubility of the potassium dipicrylamine in water and in an

excess of reagent. A saturated solution of the salt in water was prepared at 25° and 0° C. By colorimetric analysis the solubilities were found to be 0.88 and 0.073 gram per liter, respectively. In order to get an idea of the losses by solubility under conditions at which a quantitative determination may be carried out, the following experiments were made:

a. An accurately weighed amount of the potassium salt (about 0.1 gram) was placed in a sintered-glass crucible and 50 ml. of 1.5 per cent magnesium dipicrylamine solution delivered from a pipet were drawn through slowly at room temperature. The precipitate left was washed with 0.5 ml. of ice water, dried at 110° C., and weighed. The loss in weight corresponded to 0.14 gram per liter of reagent at room temperature ( $25 \pm 1^\circ \text{C}.$ ).

b. Seventy-five milliliters of a 0.5 per cent solution of magnesium dipicrylamine were added to a beaker which had been weighed together with 0.1000 gram of the potassium salt and a small porcelain filter stick. The solution was stirred at frequent intervals for 2.5 hours. The liquid was removed by suction, etc. The loss in weight corresponded to 0.25 gram per liter of 0.5 per cent reagent.

c. Experiment b was repeated, but the liquid was stirred with the salt at 0° C. The loss in weight was 0.028 gram per liter of 0.5 per cent reagent.

d. After preparing a saturated solution as mentioned under b, the beaker and its contents were cooled to 0° C. and left at this temperature for 2.5 hours. The loss in weight was 0.05 gram per liter of 0.5 per cent reagent.

These experiments show that the solubility increases about 10 times when the temperature is raised from 0° to 25° C. In the first series of experiments a suitable excess of reagent was added to the potassium solution, and the suspension was cooled and kept in ice water until no more precipitate separated. The precipitate was then collected on a sintered-glass crucible, washed with 1 ml. of ice water, then with a saturated solution of the potassium salt at 0° C., and finally with 1 ml. of ice water. The precipitate was dried and weighed. Using 10 mg. of potassium the results were relatively 2 to 3 per cent low. That these low results are to be attributed mainly to a rise in temperature of the wash solutions in the crucible during the washing is evidenced by the following experiments:

About 0.1000 gram of the potassium salt was placed on a sintered-glass crucible and washed with gentle suction with 25 ml. of ice water delivered dropwise from a pipet. The time of washing was about 2 minutes and the loss in weight corresponded to 0.26 gram per liter, whereas the solubility at 0° C. was found to be 0.073 gram per liter. In another experiment a weighed amount of the salt was washed with 75 ml. of the saturated solution of the potassium salt at 0° C. The loss in weight was 0.14 gram per liter. In order to limit the loss by solubility to a minimum, the suspension of the potassium salt in an excess of reagent must be cooled to 0° C., filtered, and washed with suitable wash liquids at this temperature.

Other errors, due to coprecipitation with the potassium salt, are discussed below.

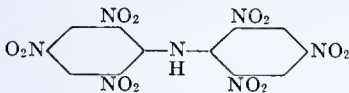
## Gravimetric Determination of Potassium

The potassium is precipitated as dipicrylamine from a neutral or slightly alkaline aqueous solution by addition of an excess of magnesium or sodium dipicrylamine. The mixture is cooled



to 0° C. and filtered with the aid of a filter stick, washed with ice water and an aqueous solution of potassium dipicrylamine which is saturated at 0° C., dried at 110° C., and weighed.

MATERIALS USED. Dipicrylamine



can be prepared according to the directions of Austens (2) or Hoffman and Dame (4) or by direct nitration of diphenylamine (1).

A product suitable for analytical purposes can be obtained from the Eastman Kodak Company, Rochester, N. Y., and was used in most of the work. It can be recovered easily by acidifying the filtrate containing the excess of reagent, and from the weighed potassium salt, by dissolving the latter in a little acetone, diluting with water, and acidifying. Caution should be observed with the acid and the reagent, as when they come in contact with the skin they may cause blisters, resembling burns that cause intense itching and heal slowly. The reagent does not cause immediate discomfort when it gets on the skin and several days elapse before the blisters appear.

The other materials used were c. p. products which were purified by standard methods when necessary. The salts used in testing the effect of their presence upon the determination of potassium were found to contain less than 0.01 mg. of potassium per gram, as indicated by the sodium cobaltinitrite test.

MAGNESIUM DIPICRYLAMINATE REAGENT: 3 per cent. Twelve grams of dipicrylamine are mixed with 5 grams of magnesium oxide and the mixture is transferred with 400 ml. of water to a 500-ml. Erlenmeyer flask. The solution is stirred well, allowed to stand for 15 to 20 hours, and filtered. The concentration of a reagent prepared in this manner can be determined by evaporating 5 ml. to dryness and weighing the residue. It was found to be 3 per cent or 0.066 N with respect to magnesium dipicrylamine. This reagent is referred to as 3 per cent reagent.

Magnesium oxide is preferred to magnesium carbonate, as the former dissolves the amine more rapidly. Heat should not be applied in the preparation of the reagent, because solutions prepared in this way tend to deposit a solid on standing. If the reagent becomes turbid, it should be filtered before use.

SODIUM DIPICRYLAMINATE SOLUTIONS: 3 per cent. Although the magnesium reagent is used in most of the determinations, the sodium reagent may be of advantage in the presence of anions which form a precipitate with magnesium. The sodium reagent is prepared by mixing the amine with a slight excess of sodium carbonate and diluting with water to give a solution which is 3 per cent in sodium dipicrylamine.

WASHING SOLUTION 1. Distilled water cooled to 0° C. by placing 50 ml. in a 100-ml. Erlenmeyer flask in an ice bath.

WASHING SOLUTION 2. A saturated solution of potassium dipicrylamine in water at 0° C. is prepared by adding an excess of the potassium salt to water in a beaker at room temperature. The beaker is placed in ice water and after standing at least a few hours the wash solutions can be drawn off through a filter stick or by pipetting off the clear supernatant liquid.

STANDARD POTASSIUM CHLORIDE SOLUTION. A solution of recrystallized and dried c. p. potassium chloride is prepared, containing 10 mg. of potassium per 5 ml. of solution.

PROCEDURE. An ordinary 30-ml. porcelain crucible containing a thin glass stirring rod and a small Emich (9) porcelain filter stick are weighed together on an analytical balance. (The diameter of the plate of the filter sticks used was 10 mm. and their height 50 mm. They may be purchased from the Fish-Schurmann Corporation, 250 East 43rd St., New York, N. Y.) A known amount of the sample is placed in the crucible and the volume so adjusted that the solution contains about 2 mg. of potassium per milliliter. If the solution is acid it is neutralized with sodium hydroxide until neutral to thymol blue; if it is alkaline it is neutralized with hydrochloric acid using the same indicator. With constant stirring 50 to 100 per cent excess of the 3 per cent magnesium reagent (for 10 mg. of potassium 7 ml. of reagent are used) is added dropwise to precipitate the potassium. The crucible containing the solution and stirring rod is cooled for at least 15 minutes in ice water and then placed in a shallow dish filled with ice water. The filter stick is mounted just above the bottom of the crucible as indicated in Figure 1, the supernatant liquid removed, and the precipitate sucked as dry as possible. The precipitate is washed once with 1 ml. of washing solution 1 (to avoid precipitation of the potassium salt by common-ion effect) then with three to four 1-ml. portions of washing solution 2, and finally with 0.5 ml. of washing solution 1. The filter stick is disconnected and placed in the crucible with the stirring rod. The outside of the crucible is wiped clean, and the crucible

and contents are dried at 110° C. for 1 hour, cooled in a desiccator, and weighed. The weight of the precipitate multiplied by 0.08194 yields the amount of potassium.

TABLE I. GRAVIMETRIC DETERMINATION OF POTASSIUM

Potassium Taken Mg.	Weight of Precipitate Gram	Potassium Found Mg.	Relative Error %
20.00	0.2439	19.98	-0.1
20.00	0.2432	19.93	-0.4
10.00	0.1215	9.95	-0.5
10.00	0.1217	9.97	-0.3
10.00	0.1220	9.99	-0.1
10.00	0.1217	9.97	-0.3
10.00	0.1218	9.98	-0.2
10.00	0.1222	10.01	0.1
10.00	0.1217	9.97	-0.3
4.95	0.0605	4.96	0.2
4.99	0.0611	5.006	0.3
1.118	0.0137	1.112	-0.5
1.006	0.0123	1.007	0.1
1.000 <sup>a</sup>	0.01202	0.984	-1.6
1.000 <sup>a</sup>	0.01199	0.982	-1.8

<sup>a</sup> In these cases the potassium salt was dissolved in 5 ml. of water and precipitated with 4 ml. of reagent.

As shown in Table I, the procedure gives satisfactory results with amounts of potassium varying between 5 and 20 mg. In the experiments with 1 mg. of potassium a semi-microbalance was used. Even with this small amount of potassium the results were gratifying.

Effect of Foreign Ions

No attempt has been made to determine potassium in the presence of rubidium and cesium, which also yield slightly soluble dipicrylamines.

AMMONIUM. Ammonium salts have to be removed, as ammonium dipicrylamine is slightly soluble. This can be done easily by boiling the solution with a slight excess of magnesium oxide until the vapors do not change the color of sensitive litmus paper. The solution is filtered, the precipitate washed, and the filtrate evaporated to the desired volume. Naturally, the magnesium oxide should be tested for the presence of potassium and a correction should be made, if necessary. In the determination of 10 mg. of potassium by the procedure in the presence of 100 mg. of ammonium added as ammonium sulfate, the results were 0.4 to 0.5 per cent high.

When the ammonium content is not too large, it may be possible to make the ammonium harmless by the addition of

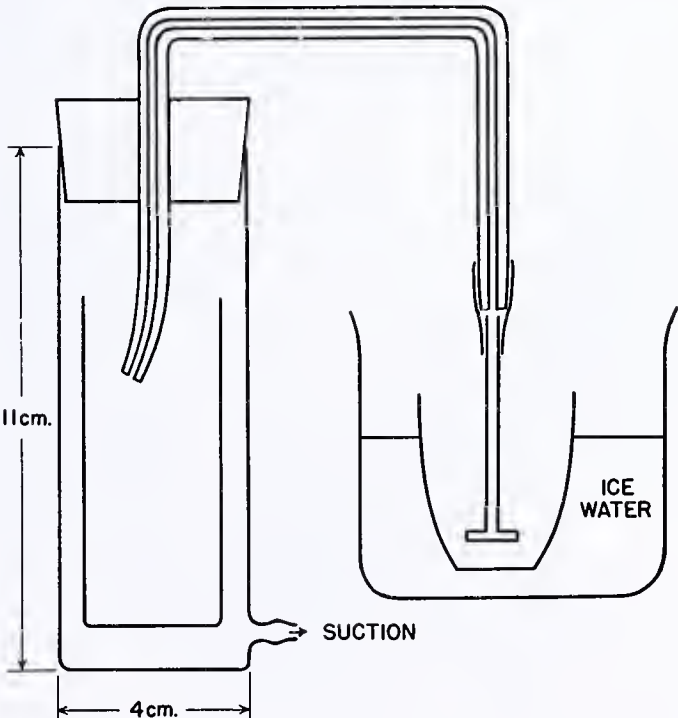


FIGURE 1. DIAGRAM OF APPARATUS



a slight excess of sodium hydroxide, as free ammonia does not give a precipitate. In this case the potassium should be precipitated with the sodium dipicrylamine solution.

TABLE II. DETERMINATION OF 10.00 MG. OF POTASSIUM IN THE PRESENCE OF SODIUM

Sodium Added Mg.	Number of Precipitations	Weight of Precipitate Mg.	Potassium Found Mg.	Relative Error %
50	1	0.1213	9.94	-0.6
55	1	0.1220	10.00	0.0
81	1	0.1217	9.97	-0.3
96	1	0.1218	9.98	-0.2
177	1	0.1240	10.16	1.6
220	1	0.1305	10.70	7.0
220	1	0.1308	10.71 <sup>a</sup>	7.1
300	1	0.1452	11.90	19.0
220	2	0.1221	10.00	0.0
240	2	0.1212	9.93	-0.7
300	2	0.1184	9.70	-3.0
500	2	0.1184	9.70	-3.0
600	2	0.1160	9.50	-5.0

<sup>a</sup> Reagent added to boiling solutions and mixture cooled. Apparently, temperature of precipitation does not affect amount of coprecipitation.

SODIUM. As the determination of potassium in the presence of sodium is of great practical importance, the effect of sodium was investigated in a fairly extensive way. Sodium was added to the solution in the form of chloride, nitrate, or sulfate; the type of anion used was found to have no effect. Some of the results are given in Table II.

In case double precipitation was used the original precipitate was filtered as described in the general procedure. After removing the excess of reagent, the precipitate was not washed but dissolved in 3 ml. of acetone. The filter stick was washed dropwise with acetone and removed from the crucible. The solution in the crucible was diluted with 5 ml. of water and 3 ml. of reagent were added (in the first precipitation 7 ml. of reagent were used). The mixture was heated on the steam bath until no odor of acetone was noticeable, cooled, and treated further as described in the procedure.

TABLE III. DETERMINATION OF POTASSIUM IN THE PRESENCE OF LARGE AMOUNTS OF SODIUM

(Modified procedure)					
Sodium Added Mg.	Number of Precipita- tions	Weight of Precipitate Mg.	Potassium Taken Mg.	Potassium Found Mg.	Relative Error %
0.0	1	0.1220	10.00	9.99	-0.1
0.0	2	0.1216	10.00	9.96	-0.4
108	1	0.1224	10.00	10.03	0.3
300	2	0.1207	10.00	9.89	-1.1
400	2	0.1184	10.00	9.70	-3.0
800	2	0.0830	10.00	6.80	-32
80 <sup>a</sup>	1	0.0119	1.000	0.975	-2.5
200 <sup>a</sup>	1	0.0150	1.000	1.23	23

<sup>a</sup> The salt mixture was dissolved in 5 ml. of water and precipitated with 4 ml. of reagent.

Table II indicates that the coprecipitation of sodium is negligibly small in the precipitation of 10 mg. of potassium in the presence of 100 mg. of sodium. Even in the presence of 180 mg. of sodium the error by coprecipitation of sodium was only 1.6 per cent. With an increasing amount of sodium the error increases rapidly, but it can be eliminated when not more than 250 mg. of sodium is present. When the amount of sodium is greater, part of this cation precipitates in the first precipitation and the precipitation of potassium becomes incomplete. By changing the general procedure it is possible to determine potassium in the presence of a slightly larger excess of sodium with a reasonable accuracy. Thus, experiments were carried out with a solution of 10 mg. of potassium in 15 ml. of water (instead of 5 ml.) to which 10 ml. of 3 per cent magnesium reagent were added. The further treatment was as described in the general procedure. The results are given in Table III.

For the determination of traces of potassium in sodium salts special procedures should be worked out. From the

results in Table III it is seen that 1 mg. of potassium can be determined in the presence of 80 mg. of sodium with an accuracy of 2.5 per cent. When the ratio becomes still less a separation of the potassium as cobaltinitrite is advisable. The small amount of sodium in the precipitate will not interfere with the determination after destruction of the precipitate and removal of the cobalt.

TABLE IV. DETERMINATION OF POTASSIUM IN THE PRESENCE OF LITHIUM, MAGNESIUM, CALCIUM, AND BARIUM

(Potassium taken, 10.00 mg.)				
Foreign Ion Present	Amount Added Mg.	Weight of Precipitate Gram	Potassium Found Mg.	Relative Error %
Li	12	0.1218	9.98	-0.2
	50	0.1235	10.12	1.2
	109	0.1261	10.33	3.3
Mg	10	0.1219	9.99	-0.1
	50	0.1219	9.99	-0.1
	100	0.1217	9.97	-0.3
Ca	200	0.1230	10.08	0.8
	32	0.1221	10.00	0.0
	84	0.1226	10.04	0.4
Ba	170	0.1230	10.08	0.8
	320	0.1284	10.52	5.2
	6	0.1293	10.6	6.0
	27	0.1606	13.2	32.0
	52	0.1961	16.1	61.0

LITHIUM, MAGNESIUM, CALCIUM, AND BARIUM. In Table IV it is shown that the procedure gives good results in the presence of relatively large amounts of magnesium, lithium, and calcium. In the determination of 1.000 mg. of potassium in the presence of 100 mg. of calcium the error was 0.4 per cent. Barium interferes, and should be removed. Table IV shows that the error increases linearly with the barium concentration in the solutions, indicating a mixed crystal formation of potassium and barium dipicrylamines.

TABLE V. DETERMINATION OF 10.00 MG. OF POTASSIUM IN THE PRESENCE OF METALS GIVING A PRECIPITATE WITH THE REAGENT

Metals Added	Magnesium Oxide Used Gram	Potassium Found Mg.	Relative Error %
	0.2	9.95	-0.5
	0.2	9.98	-0.2
	2.0	9.78	-2.2
10 mg. each of Fe <sup>+++</sup> , Al, Cr <sup>+++</sup> , Zn, } Ni, Cu, Co, Zn }	0.2	10.03	+0.3
	0.2	10.07	+0.7
	2.0	9.90	-1.0
100 mg. each of above metals <sup>a</sup> }	2.0	9.82	-1.8
	2.0 <sup>b</sup>	10.12	+1.2

<sup>a</sup> Without addition of potassium no precipitate of potassium dipicrylamine was found after separation.

<sup>b</sup> 1 gram of magnesium sulfate was added to mixture before addition of magnesium oxide.

Experiments were also carried out with a mixture containing 10 mg. of potassium, 100 mg. of sodium, 20 mg. of lithium, and 100 mg. of magnesium. The errors found fluctuated between -0.3 and +0.3 per cent.

METALS WHICH FORM A PRECIPITATE IN ALKALINE MEDIUM interfere with the potassium determination. As relatively large amounts of magnesium do not interfere (see Table IV), the use of magnesium oxide for the removal of these cations is suggested. The results reported in Table V were obtained in the following way:

A solution of the chlorides of the metals to be separated was diluted to approximately 50 ml. in a 150-ml. beaker. A measured volume of potassium chloride solution containing 10.00 mg. of potassium and the indicated excess of magnesium oxide were added. After boiling gently for 10 minutes the suspension was allowed to cool, filtered, and the precipitate washed. The combined filtrate and washings were evaporated to about 10 ml. and transferred to a 30-ml. crucible in which the solution was evaporated to 5 ml. The potassium was precipitated by the regular procedure.

The results are satisfactory. When the ratio of potassium to other cations (100 mg. of each) is unfavorable, apparently some potassium is absorbed by the precipitate of hydrous ox-



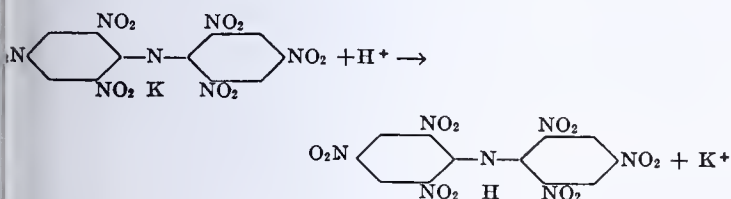
des. This adsorption can be decreased by the addition of magnesium sulfate, in which case slightly high results were found, undoubtedly due to coprecipitation of magnesium with the potassium dipicrylamine. Probably a reprecipitation of the latter would improve the results. However, the authors have not attempted to find suitable procedures for all cases which may occur.

**PHOSPHATE.** The presence of phosphate interferes when the magnesium reagent is used; the 3 per cent sodium reagent should be used instead. Determinations were made with a mixture of 10.00 mg. of potassium and 90 mg. of phosphate (as  $\text{Na}_2\text{HPO}_4$ ) using the sodium reagent. The phosphate was found to cause no interference; in the absence of phosphate the results fluctuated between  $-0.3$  and  $+0.3$  per cent, and in the presence of phosphate between  $-0.3$  and  $+0.0$  per cent. When other anions are present which precipitate with magnesium, the sodium reagent should be applied.

### Acidimetric Determination

Although the gravimetric procedure is simple and rapid, the volumetric procedure may have advantages in routine analyses.

**PROCEDURE.** The potassium is precipitated and washed as in the gravimetric procedure. The receptacle used to collect the filtrate (see Figure 1) is replaced by a clean one. With the filter stick connected with the suction apparatus, acetone is added dropwise down the sides of the crucible and the solution is drawn over into the receptacle. After all the precipitate in the crucible and on the filter stick has dissolved and the acetone remains colorless, the suction is turned off and the receptacle is removed. The acetone solution is diluted with 5 to 10 ml. of water, and heated to ensure complete solution of the potassium salt. A measured excess of standard acid is added and the receptacle is placed on a steam bath to coagulate the precipitated dipicrylamine and to remove the acetone. When no odors of acetone are noticeable, the mixture is cooled in ice water and the amine filtered off on a sintered-glass crucible and washed with ice water. The combined filtrate and washings are heated to boiling to expel carbon dioxide and, while hot, titrated with standard sodium hydroxide using bromothymol blue as indicator. The amount of acid used is equivalent to the amount of potassium in the precipitate; 1 ml. of  $0.1\ N$  acid corresponds to 3.91 mg. of potassium.



The suspension of the amine is cooled and the washing is carried out with ice water in order to minimize the amount of amine going into solution. In blank experiments 50 ml. of ice-cold water are drawn through a washed precipitate of the amine. The filtrate had a slightly yellow color but required only 0.05 ml. of  $0.1\ N$  sodium hydroxide to change the color of the indicator.

TABLE VI. GRAVIMETRIC AND VOLUMETRIC DETERMINATION OF 10.00 MG. OF POTASSIUM

Foreign Ion Present	Amount of Foreign Ion Mg.	Potassium Found Gravimetrically Mg.	Relative Error %	Potassium Found Volumetrically Mg.	Relative Error %
...	..	10.01	+0.1	9.99	-0.1
...	..	9.98	-0.2	9.97	-0.3
...	..	9.95	-0.5	10.02	+0.2
...	..	9.94	-0.6	9.95	-0.5
Na	50	9.97	-0.3	10.00	0.0
Na	96	9.98	-0.2	10.04	+0.4
Ca	18	10.00	0.0	10.02	+0.2

In the experiments with 10.00 mg. of potassium reported in Table VI, 5 ml. of  $0.1\ N$  hydrochloric acid were used to precipitate the amine and the back-titration was made with  $0.035\ N$  sodium hydroxide. In these experiments the potassium dipicrylamine was first weighed and then determined volumetrically.

Experiments have also been carried out by an indirect method. A measured excess of standard reagent was added to the solution of the potassium salt and the amount of dipicrylamine left in the filtrate and washings was determined acidimetrically. The reagent was standardized under similar conditions. This method may be of practical importance with larger amounts of potassium (20 mg. or more), but is not recommended for the determination of smaller amounts, as a fairly large excess of reagent has to be used to ensure complete precipitation of potassium. Working with 10 mg. of potassium results were accurate to about 1 per cent.

### Colorimetric Determination

The colorimetric method is particularly suitable for the determination of microquantities of potassium. The aqueous solutions vary in color from an orange-red at saturation to a light yellow at low concentrations. The light absorption of slightly alkaline aqueous solutions of the potassium salt in water at concentrations varying between 0.25 and 3.0 mg. of salt per liter was measured in a B. Lange photoelectric colorimeter using a blue filter. In Figure 2 are plotted the values of the logarithm of the percentage of transmitted light  $\log(I/I_0 \times 100)$  against the concentration, and it is seen that Beer's law does not hold for aqueous solutions of potassium dipicrylamine. Therefore, the ordinary colorimeter is not suitable for the colorimetric determination of potassium. However, one can use the photoelectric colorimeter and make a calibration curve or apply the equicolor method as in a Nessler determination or a colorimetric titration. The former method is the simplest.

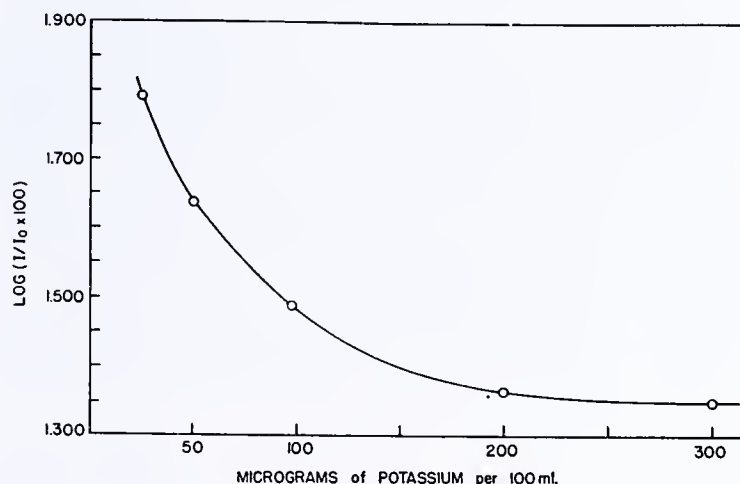


FIGURE 2

Aqueous solutions of potassium dipicrylamine are slightly hydrolyzed. In order to repress the hydrolysis completely, 1 ml. of  $0.1\ N$  sodium hydroxide was always added to 100 ml. of solution. More sodium hydroxide does not affect the light absorption. The aqueous solutions of the potassium salt are quite stable. The light absorption was found unchanged after a week of standing. It was hardly affected by the temperature—for example, a solution which absorbed 67.3 per cent at  $25^\circ\text{C}$ . was found to absorb 67.4 per cent at  $40^\circ\text{C}$ . The color of the dipicrylamine ion is intense; a solution containing 0.02 mg. of potassium salt per 100 ml. is still distinctly yellow.

The largest source of error in the determination of microquantities of potassium is the relatively large solubility. For the quantitative separation of amounts of potassium between 0.1 and 0.01 mg. the following procedure was used.

**PROCEDURE.** The solution is evaporated to dryness in a 20-ml. porcelain crucible. Three drops of the three per cent magnesium (or, if desirable, sodium) reagent are added to precipitate the



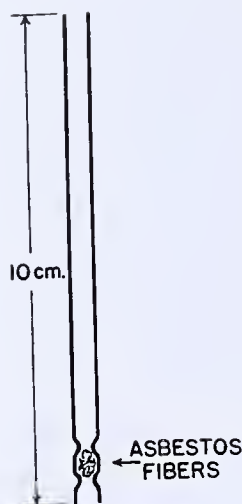


FIGURE 3

potassium, and the crucible is placed in ice water for at least 15 minutes. Without removing the crucible from the ice water the precipitate is collected on a filter stick (cooled in ice water) as shown in Figure 3. This stick consists of a 4-mm. glass tubing containing two constrictions between which asbestos fibers are placed. The mother liquor is removed by suction, and the precipitate is washed with 2 drops of ice water (washing solution 1, gravimetric procedure), then with 7 to 10 drops of washing solution 2, and finally with one drop of ice water. The filter stick is removed from the suction and the longer section of the stick is filled with acetone by means of an eye dropper. The end opposite the asbestos is placed in the mouth and the acetone is blown through the asbestos, collecting the solution in the crucible in which the precipitation has been made. This is repeated until all the precipitate has dissolved and the acetone has become colorless. The acetone solution is then diluted to 100 ml. (or any other desired volume) with water containing 1 ml. of 0.1 N sodium hydroxide per 100 ml.

TABLE VII. COLORIMETRIC DETERMINATION OF 10 TO 100 MICROGRAMS OF K<sup>+</sup>

K taken, $\gamma$	100	100	90	80	70	60	50	40	30	20	20	10
Light absorption, %	67.5	69	67.0	64.8	62.5	59.8	55.8	50.0	44.1	33.0	34.0	18.0
K found, $\gamma$	94	100	90	78	68	59	50	39	31	20	21	9
Error, $\gamma$	-6	0	0	-2	-2	-1	0	-1	+1	0	+1	-1

In the following experiments a Lange photoelectric colorimeter was used for the measurements. A calibration curve had been made with solutions of the potassium salt over a wide range of concentrations. From the light absorption of the unknown and the calibration curve the amount of potassium was found. The results given in Tables VII and VIII indicate that the method yields satisfactory results with amounts of potassium varying between 10 and 100 micrograms, even in the presence of relatively large amounts of foreign ions which do not precipitate with the reagent.

A photoelectric colorimeter is not essential for making the determination. If the unknown solution is placed in a Nessler

TABLE VIII. COLORIMETRIC DETERMINATION OF POTASSIUM IN THE PRESENCE OF FOREIGN IONS

Foreign Ion	Amount of Foreign Ion Mg	Potassium Taken $\gamma$	Potassium Found $\gamma$	Error $\gamma$
...	...	50	47	-3
...	...	50	48	-2
Na	0.5	50	48	-2
...	1.0	50	45	-5
...	3.0	50	48	-2
Mg	0.5	50	48	-2
...	1.0	50	50	0
...	3.0	50	54	+4
Li	1.0	50	50	0
Ca	1.0	50	54	+4
...	...	25	27	+2
Na	3.0	25	36	+11
Mg	1.0	25	29	+4
Li	1.0	25	29	+4
Ca	1.0	25	29	+4

tube and its color matched by adding a standard solution of the potassium salt to 0.001 N sodium hydroxide in a second tube, the amount of potassium can be calculated in the unknown. As Beer's law does not hold, the volumes when the final comparison is made should be the same. Several determinations made by this method yielded results of the same order of accuracy as obtained with the photoelectric colorimeter.

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## Colorimetric Determination of Ascorbic Acid

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RECENTLY Basu and Nath (1) reported the reduction of 2,6-dichlorophenolindophenol by ferrous salts in the presence of dibasic and hydroxy organic acids. Similarly Lorenz and Arnold (2) show the interference of the ferrous ion on the dye. Some time ago, A. J. Lorenz advised the authors that work from the California Fruit Growers Exchange laboratories indicated that "most canned citrus juices showed about 40 p. p. m. tin, and some iron, tin affecting the iodine titration and iron the 2,6 dye." A representative of the National Canners Association has advised that "no chemical preservatives are required and none are ever used" in canned grape-

fruit juice, and that "heat constitutes the sole means of preservation in canned foods." The statement made by the authors (3) "the higher values obtained for the canned sample of grapefruit juice may be due to preservatives" is therefore misleading. The above information is submitted as a possible source for the explanation of the discrepancy observed between them.

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# Reaction between Amines and Sodium 1,2-Naphthoquinone-4-Sulfonate

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THE fact that sodium 1,2-naphthoquinone-4-sulfonate yields colored solutions with compounds containing amino groups (2, 5, 9, 11, 16, 17) constitutes the basis of the Folin method for the colorimetric determination of the amino acid content of blood and urine (6, 7). No quantitative data are available, however, as to the amount of color given by this reagent with various aliphatic and aromatic amines, although these compounds frequently accompany the amino acids in biological media. When this information became of importance in connection with studies involving the concentration of certain nitrogenous constituents in blood and urine, the present investigation was undertaken. Folin's amino acid procedure has enjoyed a wide usage in biochemical fields (1, 8, 12). Certain divergent findings (4, 10, 15), however, which Danielson (3) contends result from the limited range in the proportionality due to the presence of a strong residual blank, have been reported. Hence Danielson (3) utilizes a strongly acid bleaching reagent in his modification of the original Folin method. An investigation of the factors which influence the shade and amount of color given by these procedures with various amines is reported in the present paper.

## Material and Procedure

The aliphatic amines were generally analyzed by adding a weighed portion to water and titrating to methyl red with standard acid. The aromatic amines were usually repurified by commonly accepted procedures. A carefully weighed sample of the compound being studied was diluted to a definite volume with distilled water. Occasionally a few drops of acid were necessary to render the compound water-soluble. Aliquot portions of stock solution were diluted with water to yield solutions containing quantities of nitrogen ranging from 0.042 to 0.112 mg. per 5 cc. The standard for comparison in these cases was glycine. For the Folin method the usual stock glycine solution was diluted to give a standard in 0.02 *N* hydrochloric acid, containing 0.07 mg. of nitrogen per 5 cc. The glycine standard for the Danielson method was prepared in 0.14 *N* hydrochloric acid, 5 cc. also containing 0.07 mg. of nitrogen.

## Influence of Alkalinity and Acidity

A 5-cc. sample of the glycine standard was made definitely pink with phenolphthalein by the addition of 1 cc. of the sodium carbonate reagent. Two cubic centimeters of the borax solution were added in the Danielson procedure. To a series of tubes each containing 0.07 mg. of amine nitrogen, or a multiple thereof if the nitrogen group of the compound being studied was not completely reactive, varying quantities of the alkalis were added, the contents were diluted to 10 cc. with distilled water, 2-cc. portions of freshly prepared 0.5 per cent quinone reagent were added, and the tubes were stoppered and placed in the dark for about 24 hours. The acid bleaching reagents were then added, and the contents were diluted to 25 cc. and matched against the appropriate glycine standards in the colorimeter.

Although a certain degree of alkalinity was found necessary, excess frequently resulted in a marked reduction in the amount of color produced in the reaction. Folin's carbonate solution was found to be more color-depressing, generally, than Danielson's borax reagent. Ammonium hydroxide and certain aliphatic amines, particularly methylamine, ethylamine, isopropylamine, *D*-glucosamine, etc., were extremely

sensitive and the amount of color produced with the quinone reagent decreased rapidly with increased alkalinity. Most of the aromatic amines gave highly colored; insoluble reaction products, but those which could be studied quantitatively did not seem to be greatly influenced by variations in alkalinity.

When the naphthoquinonesulfonic acid reagent was added to a faintly alkaline solution of a compound containing a reactive amino group a deep blackish brown color rapidly developed, especially in the presence of sodium carbonate. Upon acidification the color of the solutions generally became reddish brown. While studying the quinone reaction with certain aliphatic amines, however, the author noticed that the addition of the strong hydrochloric acid bleaching agent used in the Danielson method made the deep blackish brown solutions of certain amines turn such a light yellow, instead of the expected orange-red or reddish brown, that a match with the brown glycine standard was obviously impossible. Upon re-alkalization the original blackish brown color was regained; hence the colored quinone-amine condensation product had not been destroyed by the acid bleaching agent. The addition of the acetic acid-acetate solution in the Folin method always gave the expected red-brown color. This reagent never produced the light yellow color.

This difference in color production was found to be due to the fact that the Folin reaction solution, after the addition of the various reagents and dilution to 25 cc., had a pH of about 3.2, whereas the corresponding Danielson solution had a pH below 1.2. This difference in hydrogen-ion concentration, in those cases in which the naphthoquinonesulfonic acid-amine condensation product proved to be an indicator compound, was sufficient to alter markedly the color of the resultant solution. Thus *n*-butylamine, *n*-heptylamine, benzylamine, anisidine, aminobenzoic acid, etc., gave insoluble products readily removable by filtration. When these precipitates were dissolved or suspended in alcohol and then added in small quantities to a series of tubes containing buffer solutions ranging from pH 0 to pH 14, many proved to be indicator compounds frequently with two transition intervals. Thus they yielded solutions which were generally yellow from pH 0 to pH 2 and from pH 12 to 14, the intervening color being usually reddish brown or orange-red. Obviously Danielson's method cannot be used to determine the concentration of amines without further modification of the acid bleaching reagent. However, none of the products studied had transition intervals in the region covered by the Folin acetic acid-acetate reagent; hence no error of this type was introduced by this solution.

**QUANTITATIVE NATURE OF REACTION BETWEEN NAPHTHOQUINONESULFONIC ACID REAGENT AND AMINES.** From a fresh aqueous stock solution of the compound being studied aliquot portions were accurately diluted to volume with distilled water, yielding a series of solutions whose nitrogen content generally ranged from 0.042 to 0.112 mg. per 5 cc. of solution. The previously determined optimal amount of alkali was added to 5-cc. portions and the contents were diluted to 10 cc. and treated with 2 cc. of freshly prepared 0.5 per cent naphthoquinonesulfonic acid reagent. The stoppered tubes were placed in the dark and 24 hours later treated with the desired amounts of the acid and thiosulfate solutions, followed by dilution to 25 cc. The unknown solutions were then matched in the colorimeter against the usual glycine standards which generally contained 0.07 mg. of nitrogen.



TABLE I. QUANTITATIVE NATURE OF THE REACTION BETWEEN VARIOUS AMINES AND SODIUM 1,2-NAPHTHOQUINONE-4-SULFONATE

Compound Studied	Carbonate Solution Added	Folin Colorimetric Method					Color match with glycine	Danielson Modification of Folin Method		
		Mg. of Nitrogen per 5 Cc. of Solution						Borax solution added	Acid formaldehyde	Nitrogen recovered
		0.042 mg.	0.056 mg.	0.070 mg.	0.084 mg.	0.112 mg.				
		Nitrogen Recovered								
Cc.	%	%	%	%	%	Cc.	Cc.	%		
Allylamine	0.5	111.2	98.2	100.0	96.5	96.9	Good	0.8	1.0	98.7
<i>o</i> -Aminophenol	0.5	133.3	119.1	125.0	...	125.0	Fair, more orange	1.0	2.0	117.7
<i>m</i> -Aminophenol	0.4	141.2	152.5	154.0	151.6	143.3	Fair, more orange	2.0	2.0	154.0
<i>p</i> -Aminophenol	0.6	208.4	208.5	200.0	208.3	186.5	Fair, more orange	1.0	2.0	200.0
Ammonium hydroxide	0.4	93.3	103.6	95.9	83.3	89.6	Poor, too red	0.8	2.0	101.0
<i>sec</i> -Butylamine	0.6	...	53.2	50.5	46.5	43.3	Fair, too yellow		Acid-sensitive	
Isobutylamine	0.4	87.7	71.8	60.6	59.5	55.5	Poor, too yellow		Acid-sensitive	
Cadaverine dihydrochloride	0.4	115.0	104.1	99.0	92.6	76.2	Fair	0.3	0.8	97.9
Di- <i>n</i> -amylamine	0.6	123.6	112.7	102.0	104.3	94.0	Fair, too orange		Acid-sensitive	
Di- <i>n</i> -butylamine	0.7	133.3	118.6	101.1	92.6	74.4	Fair, too orange		Acid-sensitive	
Diisobutylamine	1.0	61.7	56.8	52.0	45.0	37.9	Good		Acid-sensitive	
Diethanolamine	0.3	104.3	89.3	83.3	72.5	62.5	Good	0.5	0.1	76.9
Diethylamine	0.7	119.1	104.1	97.6	93.7	72.7	Fair		Acid-sensitive	
Di- <i>n</i> -propylamine	0.8	113.8	110.0	106.1	104.2	90.6	Fair, too orange		Acid-sensitive	
Diisopropylamine		No reaction							No reaction	
Ethanolamine	0.6	119.0	109.2	102.9	96.5	91.9	Good	1.0	2.0	100.3
Ethylamine	0.2	54.3	53.2	50.1	46.3	45.6	Good	0.3	0.4	50.8
Ethylenediamine		No reaction							No reaction	
<i>d</i> -Glucosamine hydrochloride	0.1	100.4	95.3	96.4	87.9	78.1	Good	0.2	2.0	96.1
Methylamine	0.2	107.1	105.3	100.0	97.6	96.4	Perfect	0.2	2.0	97.4
Propanolamine	0.2	133.3	131.6	137.0	138.9	138.9	Fair, more orange	0.2	2.0	132.1
<i>n</i> -Propylamine	0.2	...	...	62.6	60.4	56.8	Fair, too yellow	0.5	0.4	59.7
Isopropylamine	0.1	52.1	53.6	47.6	46.3	43.1	Poor, too yellow	1.0	0.7	55.6
Putrescine dihydrochloride	0.5	104.3	100.0	102.0	101.7	105.0	Good		Insoluble	
<i>p</i> -Sulfanilic acid	0.0	185.4	195.5	192.3	136.0	110.0	Fair, more orange	0.0	2.0	192.3
<i>o</i> -Toluidine hydrochloride	1.0	115.0	102.2	103.1	106.9	Ppt.	Good		Insoluble	
Tyramine hydrochloride	0.5	110.5	119.1	111.0	104.2	104.2	Fair, more red	1.5	2.0	99.0

The data on the reaction with 27 different compounds are given in Table I and include the optimal amount of alkali and acid reagents, the per cent of nitrogen recovered, and the color match with glycine. Complete data for the Folin method only are reported. In evaluating the quantitative nature of the reaction one should utilize particularly the data in column 5 and 11 of Table I, where the per cent nitrogen recovery is given when the amine samples and the glycine standards have the same amount of nitrogen—namely, 0.070 mg. This precaution is necessary, since the data indicate that the reaction shows poor proportionality.

While the data show a certain uniformity, in that equimolecular quantities of ammonium hydroxide and 11 of the 26 reactive amines studied gave the same amount of color with the naphthoquinone reagent as an equivalent amount of glycine, certain irregularities are likewise present. Whereas the aliphatic secondary amines, ammonium hydroxide, and certain primary amines such as methylamine, allylamine, and ethanolamine reacted fully with the reagent, ethylamine, *n*-propylamine, *sec*-butylamine, and most of the other primary aliphatic amines yielded only one-half the expected amount of color. Presumably only one of the hydrogen atoms of the amino group of these compounds entered into the reaction. The color given by these derivatives was somewhat more yellow, whereas that given by the secondary amine derivatives was slightly more red or orange than that given by the glycine derivative. Steric hindrance probably accounts for the fact that diisopropylamine and ethylenediamine were completely nonreactive. On the other hand, cadaverine and putrescine resulted in quantitative color production.

In addition, the higher aliphatic amines, such as *n*-butylamine, isoamylamine, *n*-heptylamine, 2-aminoöctane, etc., gave insoluble orange-red precipitates. Tertiary amines of course did not react. Although *p*-aminophenol and *p*-sulfanilic acid gave double the amount of color, when based on an amount of nitrogen equivalent to that present in the glycine standards, most of the aromatic amines studied, such as benzylamine, *o*-, *m*-, and *p*-nitroaniline, anisidine, indole, etc., also gave insoluble reaction products. The Folin method and the Danielson modification tend to give similar results unless the 1,2-naphthoquinonesulfonic acid derivative is sensitive to Danielson's strongly acid formaldehyde solution. Although most of the compounds reacted only in the presence of

alkali, certain aromatic amines were found to react with the naphthoquinone reagent equally well in slightly acid solution. This fact enabled the author to develop methods for the determination of sulfanilamide in blood (13) and in cerebrospinal fluid (14).

The following compounds were completely nonreactive by both the Folin method and the Danielson modification: skatole, guanidine carbonate, hexamethylenetetramine, phenylhydrazine, glycoxyamine, melamine hydrochloride, adenine, guanine, xanthine, uracil, hypoxanthine, theobromine, caffeine, phenylurea, urethane, acetanilide, carbanilide, acridine, acetyl anisidine, acetyl phenol, and alloxan.

### Summary

The amount of color given by a series of amines which react with sodium 1,2-naphthoquinone-4-sulfonate was found to be influenced by the quantity of alkali and acid added to the reaction medium.

The quantitative nature of the reaction was studied by comparing the amount of color given by ammonium hydroxide and 26 different aliphatic and aromatic amines with that given by an equivalent quantity of glycine.

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# Sensitivity of the Carbonate Test for Lithium

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THOUGH lithium carbonate is mentioned as a characteristic slightly soluble lithium compound in comprehensive works on qualitative analysis, no previous investigation appears to have been made of the sensitivity of a qualitative test based upon the precipitation of lithium as the carbonate. From the solubility of lithium carbonate in water at room temperature (1.31 grams per 100 ml. of solution at 20° C. according to Mellor, 1), one would expect that such a precipitation test would be very insensitive when performed by adding a sodium carbonate solution to a solution of a lithium salt at ordinary temperatures. Experiment showed this to be the case. For example, the addition of 1 ml. of sodium carbonate reagent of any concentration to 1 ml. of lithium chloride solution containing 10 mg. of lithium was found to cause no precipitation at room temperatures. On the other hand, on heating such a mixed solution to 100° C. an abundant precipitation of lithium carbonate resulted, as might be expected from the marked decrease in the solubility of lithium carbonate with rise in temperature (1). By performing the test at this elevated temperature considerably less than 10 g. of lithium can be detected, as is shown in Table I.

TABLE I. PRECIPITATION OF LITHIUM CARBONATE BY SODIUM CARBONATE SOLUTIONS

(From pure lithium chloride solutions at 100° C.)					
Lithium Present Mg.	Lithium Solution Ml.	Reagent Solution Ml.	Appearance or Nonappearance of Precipitate with Reagent of Stated Normality		
			N	2 N	3 N
10	1	1	+	+	+
10	1	2	+	+	+
10	2	1	+	+	+
10	2	2	+	+	+
10	2	3	+	+	+
10	1	5	+	+	+
10	5	1	-	-	-
5	1	1	+	+	+
5	1	2	-	+	-
5	1	3	-	-	-
4	1	1	-	+	+
4	1	2	-	-	-
3	1	1	-	+	-
3	1	2	-	-	-
2	1	1	-	-	-
2	1	2	-	-	-

Table I shows clearly the need for closely restricting the volumes of the reacting solutions. A certain optimum concentration of sodium carbonate is required for best results. That potassium carbonate is a slightly less sensitive reagent than sodium carbonate in solutions of equivalent concentration is shown by Table II.

TABLE II. PRECIPITATION OF LITHIUM CARBONATE BY 2 N POTASSIUM CARBONATE

(From pure lithium chloride solutions at 100° C.)			
Lithium Present Mg.	Lithium Solution Ml.	Reagent Solution Ml.	Appearance or Nonappearance of Precipitate
10	1	1	+
10	1	2	+
10	2	1	+
10	2	2	+
10	2	3	+
10	1	5	+
10	5	1	-
5	1	1	+
5	1	2	-
4	1	1	+
4	1	2	-
3	1	1	-
3	1	2	-

Table III shows the influence of various concentrations of sodium or potassium ion on the sensitivity of this test. In each of these experiments the volume of the test solution is 1 ml., and 1 ml. of reagent was used. It will be seen that

a high concentration of sodium ion has very little adverse effect on the precipitation of lithium carbonate, whereas potassium ion in high concentration has a slightly more noticeable effect. However, neither sodium nor potassium interferes very much with this test for lithium. For the detection of lithium in the presence of other alkalies the following procedure is satisfactory:

Reduce the solution to be tested to a volume of about 1 ml., transfer to a small test tube, and add 1 ml. of 2 N sodium carbonate solution. After mixing the solutions well, stopper the test tube loosely and place it in boiling water for about 10 minutes. The presence of lithium is shown by the appearance of a white crystalline precipitate which usually adheres to the side of the test tube. Care must be taken not to prolong the test to such an extent that salts separate from the solution from evaporation.

TABLE III. PRECIPITATION OF LITHIUM CARBONATE WITH 2 N SODIUM OR POTASSIUM CARBONATE

(From lithium chloride solutions containing added sodium or potassium chloride)				
Li Present Mg.	Na Added Mg.	K Added Mg.	Reaction with Na <sub>2</sub> CO <sub>3</sub>	Given Reagent K <sub>2</sub> CO <sub>3</sub>
4	25	0	+	+
4	50	0	+	+
4	100	0	+	+
4	0	25	+	+
4	0	50	+	+
4	0	100	+	+
3	25	0	+	-
3	50	0	+	-
3	100	0	+	-
3	0	25	+	-
3	0	50	+	-
3	0	100	-	-

Though 3 mg. is the smallest amount of lithium that can be detected by this particular procedure, correspondingly smaller amounts can be detected by reduction of the volumes of the reacting solutions. However, in working with very small volumes a special technique must be employed to avoid error caused by evaporation. A convenient microchemical modification of the test is the following:

By means of a capillary pipet place one or two drops of the unknown solution in the bottom of a short length of 6-mm. glass tubing which has been sealed at one end. In a similar way introduce one or two drops of 2 N sodium carbonate solution and mix the solutions by means of a fine platinum wire. Seal off the open end of the tube as close to the liquid as possible. Place the prepared capsule in an ordinary test tube containing distilled water, heat to boiling, and maintain at the boiling point for at least 5 minutes. In the presence of a few tenths of a milligram of lithium a white crystalline precipitate will separate on the walls of the capsule.

## Interfering Substances

Ammonium salts increase the solubility of lithium carbonate to a marked extent and should therefore be removed from the solution before applying the test. Of course nearly all other cations give a precipitate with carbonate ion and thus interfere with the immediate application of the test. However, by taking advantage of the fact that lithium carbonate is the only metal carbonate which exhibits marked retrograde solubility with rise in temperature, the test may be applied after removal of other metal ions as carbonates by precipitation in cold solution. It is advisable to precipitate the interfering cations in dilute solution at around 0° C. with just a sufficient amount of dilute sodium carbonate solution. After removal of the precipitated carbonates by filtration, the solution is then concentrated by vacuum evaporation at room temperature or below. A second filtration to remove separated salts may be necessary before the lithium test can be applied to the small volume of liquid that must be used.



### Conclusions

Though the carbonate reaction for lithium is too insensitive at room temperature to be of much practical use, the increase in sensitivity when the test is performed at 100° C. is such that the reaction becomes as sensitive and useful as some other qualitative reactions. About 3 mg. is the least amount that can be detected by a macromethod, but by the application of microchemical technique a few tenths of a milligram can be detected.

The other alkalis do not interfere with the test. Ammonium salts prevent precipitation and must be removed. Nearly all other interfering cations may be conveniently removed by precipitation as carbonates in cold solution, the test then being applied to the filtrate after concentrating it to the proper volume. The carbonate test for lithium is the

most nearly specific of the known precipitation reactions for lithium, though it is not nearly so sensitive as tests based upon precipitation as aluminate, arsenate, fluoride, phosphate, stearate, or triple uranyl acetate. In spite of its comparatively low sensitivity it may be useful for establishing the presence of lithium as an essential constituent of an unknown material when a satisfactory decision as to the approximate amount present cannot be obtained by the usual flame or spectroscopic tests.

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## Determination of Carbonyl Compounds by Means of 2,4-Dinitrophenylhydrazine

### Water-Insoluble Carbonyl Compounds

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THE use of 2,4-dinitrophenylhydrazine in the qualitative identification of carbonyl compounds has been developed extensively by Allen (1), Brady (2), and Campbell (3), and its use as a quantitative reagent has been reported frequently for individual carbonyl compounds (4, 6, 7) and for a group of water-soluble carbonyl compounds by Iddles and Jackson (5).

Since many carbonyl compounds are insoluble or only slightly soluble in water, it seemed desirable to extend the earlier study (5) to include other carbonyl compounds which may be dissolved in alcohol. Consequently the present report is concerned with a study of the best conditions for the quantitative precipitation of certain alcohol-soluble carbonyl compounds as their 2,4-dinitrophenylhydrazones.

### Experimental

In adapting the previous work in aqueous solutions to carbonyl compounds soluble in alcohol, preliminary trials were run on a representative alcohol-soluble ketone, acetophenone, to determine (1) the effect of temperature on the completeness of reaction and (2) the final dilution necessary to ensure a quantitative precipitation of the hydrazone.

In the determination of carbonyls reported from this laboratory, the temperature was held at 0° C. This led to the suggestion by Perkins and Edwards (6) that some occlusion of the reagent might occur when the reagent was saturated at room temperature but was used in a reaction which was cooled down to 0° C. To test this point three parallel trials were made as shown in Table I, in one of which the reagent was saturated at 0° C. and the run made at the same temperature, and in the others the reagent was saturated at room temperature and the runs were made at 0° C. and at room temperature.

The close agreement of the results shown in Table I indicates that the reagent was used up by the reaction sufficiently to compensate for any decrease in its solubility when a lower temperature was employed. In another test 50 ml. of precipitating reagent (saturated at room temperature) and 10 ml. of water, the minimum volume of carbonyl solution previously used, were mixed and cooled to 0° C. No precipitate

was produced, showing that the dilution effect was sufficient to prevent precipitation of the reagent and any resulting occlusion. From these data it was concluded that determinations could be made at 0° C. or at room temperature. However, room temperature was selected for all later runs, as it offered the advantages of better particle size of precipitates, greater ease of filtration, and sufficiently low solubility of the hydrazones formed.

In determining the effect of dilution upon the precipitation of the hydrazones, trials were made in which 0, 50, and 100 ml. of 2 N hydrochloric acid were added after precipitation.

TABLE I. DETERMINATION OF ACETOPHENONE

	Volume of 2,4-Dinitro- phenylhy- drazine ML.	Volume of Sample ML.	Sample Gram/ml.	Precipitation %
Reagent saturated at 0° C. Determination made at 0° C.	30	10	0.006072	99.1
	30	10		99.8
	30	10	0.00647	99.9
	30	10		99.3
Reagent saturated at room temperature. Determination made at 0° C.	30	10	0.006072	99.9
	30	10		99.7
	30	10	0.00647	99.9
	30	10		99.1
Reagent saturated at room temperature. Determination made at room temperature	30	10	0.00647	99.4
	30	10		99.75

TABLE II. EFFECT OF DILUTION IN THE DETERMINATION OF ACETOPHENONE

Volume of 2,4-Dinitro- phenylhy- drazine ML.	Volume of Carbonyl <sup>a</sup> ML.	Volume of 2 N Hydro- chloric Acid ML.	Total Volume ML.	Precipitation %
30	10	...	40	99.0
30	10	...	40	98.6
30	10	50	90	99.1
30	10	50	90	98.1
30	10	100	140	98.8
30	10	100	140	98.6

<sup>a</sup> 0.0647 gram per 10 ml.



TABLE III. DETERMINATION OF CARBONYL COMPOUNDS AS 2,4-DINITROPHENYLHYDRAZONES

		Volume of Hy- drazine	Volume of Carbonyl	Sample	Weight of Hy- drazone	Precipi- tation			Volume of Hy- drazine	Volume of Carbonyl	Sample	Weight of Hy- drazone	Precipi- tation
		Ml.	Ml.	Gram/ml.	Gram	%			Ml.	Ml.	Gram/ml.	Gram	%
Acetophenone (b. p. 202° C.)	30	10	0.006072	0.1517	99.9	Mesityl oxide (b. p. 130° C.)	35	10	0.1624	93.9			
	30	10		0.1515	99.8		35	10		0.1640	94.8		
	30	10		0.1520	100.05		28	10		0.1620	93.7		
	30	10		0.1520	100.05				Av.	93.2			
	30	10		0.1500	98.9		Benzalacetophenone (m. p. 55.1° C.)	10	10	0.002028	0.0360	96.8	
	30	10		0.1502	99.2			10	10		0.0368	99.0	
	30	10		0.1505	99.3			15	10		0.0374	100.6	
	30	10		0.1512	99.7			7.5	10		0.0362	97.45	
	30	10	0.00647	0.1618	100.05					Av.	98.5		
	30	10		0.1615	99.9			Benzil (m. p. 95° C.) <sup>c</sup>	40	10	0.007826	0.1413	97.5
	30	10		0.1601	99.1				40	10		0.1416	97.6
	30	10		0.1604	99.3				40	10		0.1421	98.0
	30	10	0.1611	99.7					Av.	97.7			
	30	10	0.006246	0.1598	98.7		Benzophenone (m. p. 47-48° C.)		18.5	10	0.004218	0.0807	96.2
	30	10		0.1554	100.0				23	10		0.0807	96.2
	30	10		0.1554	100.0				23	10		0.0782	94.5
30	10	0.1555		100.0					Av.	95.6			
	30	10		100.0									
			Av.	99.6	Piperonal (m. p. 37° C.) <sup>d</sup>	55		10	0.013837	0.3128	102.6		
<i>p</i> -Hydroxybenzaldehyde (m. p. 116-117°)	30	10	0.006	0.1521		96.7		75		10	0.3156	103.2	
	30	10		0.1523		96.9		75		10	0.3184	104.3	
	30	10		0.1514		96.2	55	10		0.3166	103.8		
	At room temperature	30		10		0.1516	96.3				Av.	103.5	
	30	10		0.1530	97.2	Cyclohexanone (Eastman) redistilled four times	80	10	0.01	0.2761	97.4		
At 0°	25	10	0.005324	0.1313	99.8		80	10		0.2748	96.9		
	25	10		0.1312	99.75		80	10		0.2753	97.1		
				Av.	97.6		80	10		0.2751	97.0		
Benzoin (m. p. 137° C.) <sup>a,b</sup>	25	10	0.002885	0.0537	100.80		80	10		0.2762	97.4		
	25	10		0.0539	100.95		80	10		0.2765	97.50		
	25	10		0.0537	100.80	80	10	0.2769	97.63				
	25	10		0.0532	99.75			Av.	97.3				
	25	10		0.003719	0.0681	99.0	Cyclopentanone (Eastman) redistilled four times	53	10	0.007537	0.2316	98.0	
	25	10	0.0678		98.7	53		10	0.2324		98.5		
	15	10	0.0666		97.0	53		10	0.2318		98.0		
	15	10	0.0686		99.8	71		10	0.2331		98.6		
			Av.		99.6	71		10	0.2324		98.5		
	Mesityl oxide (b. p. 130° C.)	35	10	0.006503	0.1687	91.5		Carvone (Eastman) redistilled four times	56	10	0.01	0.2072	98.76
35		10	0.1691		91.8	56			10	0.2084		99.33	
35		10	0.1725		93.5	42			10	0.2091		99.71	
35		10	0.1731		93.9	42			10	0.2084		99.34	
35		10	0.006108		0.1604	92.2			42	10		0.2093	99.76
							Av.		99.38				

<sup>a</sup> Reaction incomplete at 0° C.  
<sup>b</sup> Only a hydrazone, as shown by Rabassa (?).  
<sup>c</sup> Calcd. on basis of monohydrazone.  
<sup>d</sup> Large crystals of hydrazone with occlusion.

<sup>a</sup> Reaction incomplete at 0° C.  
<sup>b</sup> Only a hydrazone, as shown by Rabassa (?).  
<sup>c</sup> Calcd. on basis of monohydrazone.  
<sup>d</sup> Large crystals of hydrazone with occlusion.

As shown in Table II, there is no apparent effect produced by further decreasing the concentration of alcohol beyond the dilution caused by the aqueous reagent itself.

From all the experimental trials on acetophenone the optimum conditions selected for a general procedure were as follows:

A known weight of the purified carbonyl compound was diluted to 100 ml. with aldehyde- and ketone-free 95 per cent ethyl alcohol. Ten-milliliter aliquot portions of this stock solution were added dropwise, with continuous stirring, to a volume of the 2,4-dinitrophenylhydrazine reagent (a saturated solution in 2 *N* hydrochloric acid) equivalent to 50 to 100 per cent excess of that theoretically required for complete precipitation. The precipitated solutions were usually diluted by addition of 50 ml. of 2 *N* hydrochloric acid and allowed to digest at room temperature or 2 to 24 hours. The precipitates were then filtered onto tared Gooch crucibles, washed with 100 to 150 ml. of 2 *N* hydrochloric acid, then with distilled water until the washings gave no test with silver nitrate, and dried in an oven at 105° to 110° C. to constant weight.

This procedure was used to study the completeness of precipitation of the 2,4-dinitrophenylhydrazones of acetophenone, *p*-hydroxybenzaldehyde, benzoin, mesityl oxide, benzalacetophenone, benzil, benzophenone, piperonal, cyclohexanone, cyclopentanone, and carvone. The results are tabulated in Table III and show a very satisfactory efficiency of recovery for organic quantitative precipitations.

### Conclusions

Supplementing an earlier study (5) on water-soluble carbonyl compounds, the authors have sought to determine the optimum conditions for the quantitative estimation of

alcohol-soluble carbonyl compounds as their 2,4-dinitrophenylhydrazones. In the experimental determinations a sample containing a small quantity of the carbonyl compound in alcoholic solution was added to an excess of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid and the reaction mixture was allowed to stand at room temperature after dilution with 50 ml. of 2 *N* hydrochloric acid. The precipitate was filtered, washed with 2 *N* hydrochloric acid and water, and dried at 105° to 110° C. to a constant weight.

Determinations of the amounts of hydrazone produced from samples of eleven aldehydes and ketones were made and compared with the known theoretical values with variations of -0.4 per cent for acetophenone, -2.4 per cent for *p*-hydroxybenzaldehyde, -0.4 per cent for benzoin, -6.8 per cent for mesityl oxide, -1.5 per cent for benzalacetophenone, -2.3 per cent for benzil, -4.4 per cent for benzophenone, +3.5 per cent for piperonal, -2.7 per cent for cyclohexanone, -1.4 per cent for cyclopentanone, and -0.62 per cent for carvone.

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# Determination of Beta-Carotene in Alfalfa Meals

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THE importance of alfalfa meals as a source of carotene for commercial feed mixtures has necessitated the development of an analytical technique suitable for routine analysis. Four methods useful for this purpose have been studied (1, 2, 4, 5) and from experience with these a comparatively rapid and satisfactory procedure has been developed. Five outstanding advantages distinctly in favor of this technique are: (1) 125-cc. separatory funnels are employed, and proportionately small amounts of solvents and reagents used; (2) twelve or more determinations may be run simultaneously; (3) ten to twelve water washings are eliminated; (4) concentration of the petroleum ether extract is unnecessary; and (5) the photometer is used in place of a colorimeter.

A special type of shaker (Figure 1), which has been developed in this laboratory, for the determination of carotene in alfalfa meals, greatly facilitates the many extractions and washings required.

The shaking apparatus consists essentially of a shaker rack and a shaker carriage geared at right angles to a 0.16-horsepower General Electric motor (Figure 2). The shaker rack is hinged to the carriage in such a way that it may be brought to an upright position after each shaking operation (Figure 3). The shaker rack is constructed from 1.25-cm. (0.5-inch) stock braced with 0.6-cm. (0.125-inch) plywood; 125-cc. separatory funnels rest in rubber collars in holes having a diameter of 3.75 cm. (1.5 inches). During the process of shaking, the glass stoppers of the separatory funnels are securely held in place by a hinged toppiece, the wing of each stopper passing through a slot in the

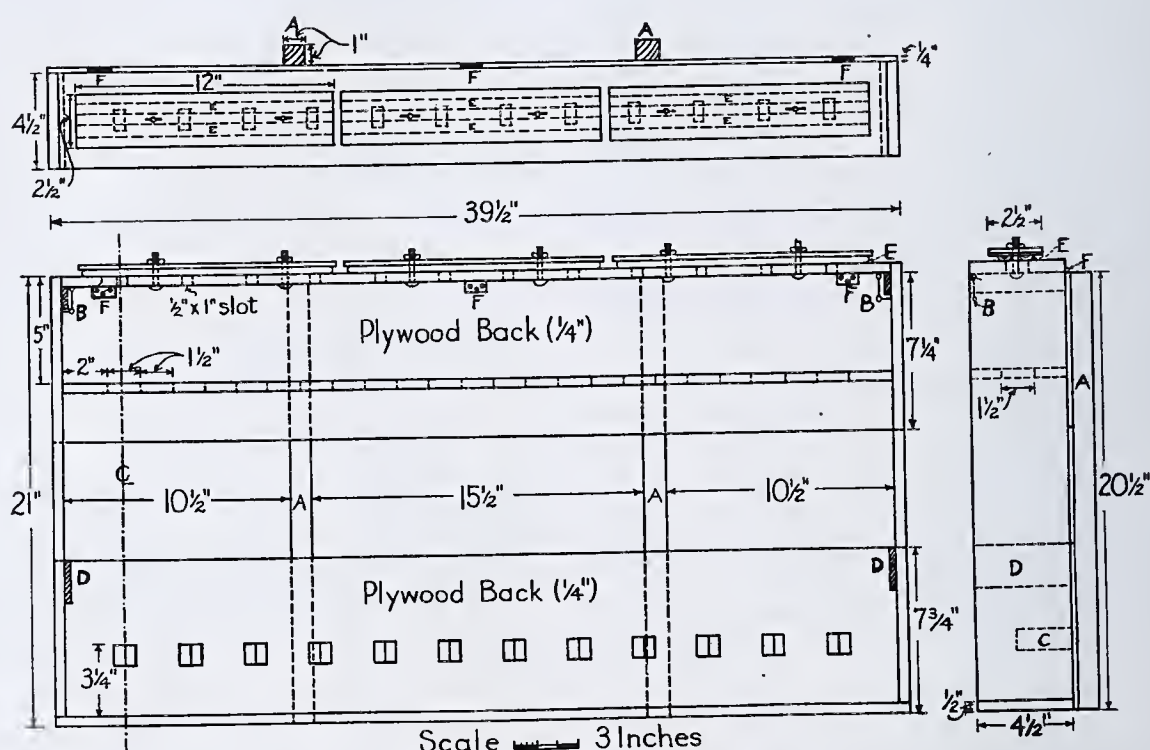


FIGURE 1. DIAGRAM OF SHAKER

A. Cleats for shaker carriage  
B. Hook fastener

C. Clamp for flask  
D. Cleat for funnel rack (Figure 4)

E. Rubber tubing (1.25-cm.)  
F. Hinge

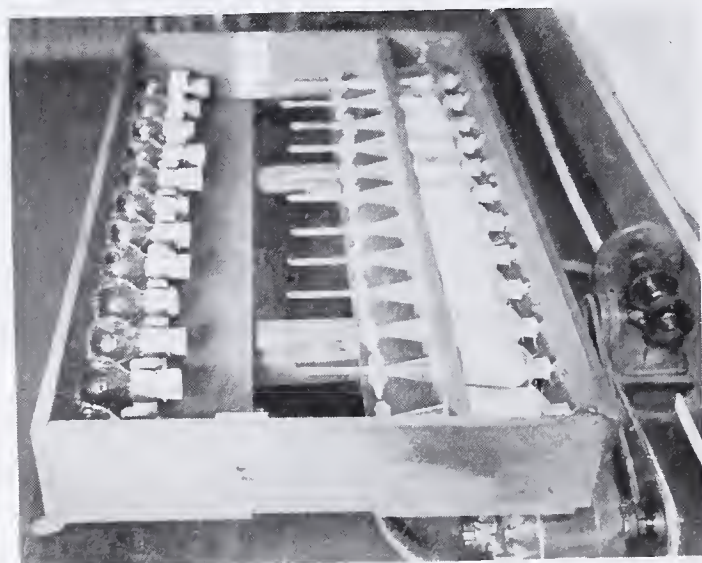


FIGURE 2. SHAKER AND MOTOR

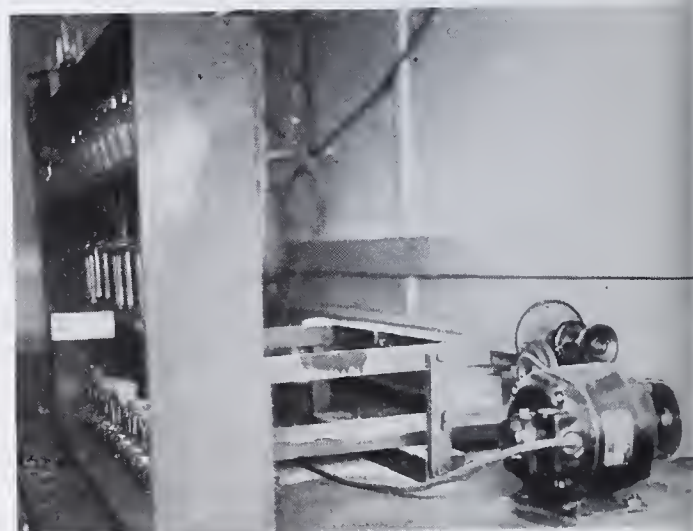


FIGURE 3. MOTOR AND UPRIGHT SHAKER



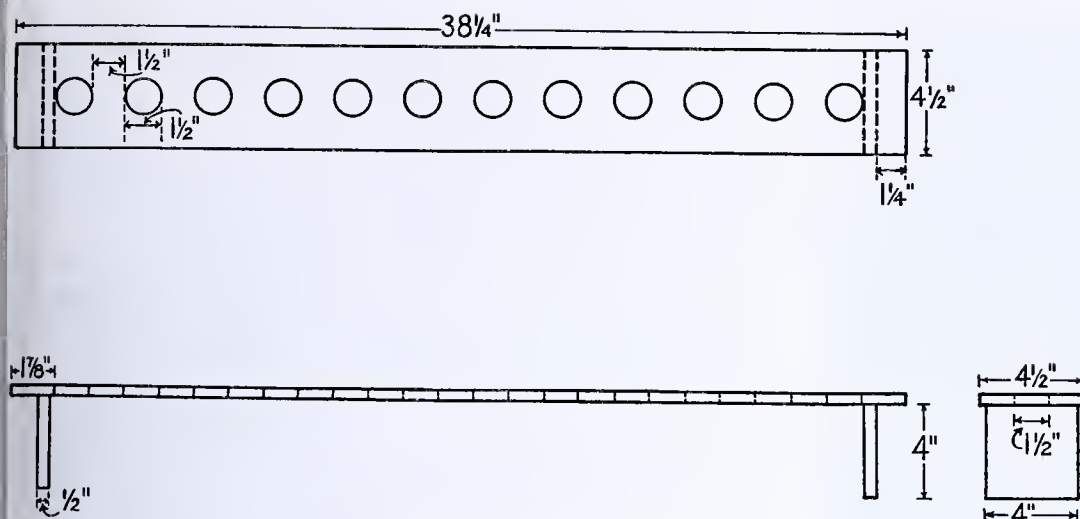


FIGURE 4. FUNNEL RACK

piece. Strips of plywood, held in place by bolts and adjustable by wing nuts, secure the stoppers.

Lengths of 1.25-cm. (0.5-inch) rubber tubing attached to the under side of the plywood strips facilitate adjustment. Very little adjusting is necessary once the apparatus is assembled. Phosphor bronze clamps are used to hold 100-cc. extraction flasks in place. A rack for holding the glass funnels, used in transferring the petroleum ether extract into the separatory funnels, is a great convenience (Figures 4 and 5), and may also be used in the final filtration of the carotene solution into volumetric flasks (Figure 5, lower).

### Determination

Weigh 2 grams of finely ground alfalfa meal into a 100-cc. extraction flask, add 15 cc. of 10 per cent solution of potassium hydroxide in 95 per cent ethanol, and wash down the sides of the flask with about 5 cc. of 95 per cent ethanol. It is best to filter the alcoholic solution before use. Attach the flask to a reflux condenser and boil the contents (Figure 6) for 30 minutes. It is advisable to lift and rotate the flask occasionally to keep the sample from lumping. Remove the flask and cool quickly to room temperature.

Add 15 cc. of petroleum ether to the flask and cork tightly. Place in a clamp on the shaker (Figure 5, upper), lower the shaker rack onto the carriage, and shake for 2 minutes. Rotate the flask occasionally by hand while shaking. Elevate the shaker to the perpendicular position and filter the supernatant liquid to the separatory funnel through a short-necked glass funnel (2.5 cm., 2.5 inches, in diameter) containing a small loose plug of nonabsorbent cotton (Figure 5, center). Grease and secure the stopper of the separatory funnel. The stoppers of the separatory funnels must be frequently greased during the whole procedure. After three extractions, add 10 cc. of 95 per cent ethanol to break up the residue, and then extract with 15-cc. portions of petroleum ether as above until the extractions are colorless. Six extractions in all usually suffice, although this will vary according to the sample.

Remove the filter rack, fill the separatory funnel with distilled water, and allow to stand for 15 minutes. Slowly drain the water layer almost completely, leaving about 1 cc. to act as a seal.

Add a 20-cc. portion of distilled water to the separatory funnel, secure the stopper as described above, lower the shaker rack onto the carriage, and shake for 2 minutes. Elevate the shaker rack and run off the water layer. After this single washing with water, wash the solution repeatedly with 20-cc. portions of 89 per cent methanol until the methanol remains water-white and is found to be free of alkali. Finally filter the petroleum ether extract directly into 100-cc. volumetric flasks through S. & S. No. 597 11-cm. paper on which has been placed 1 gram of anhydrous sodium sulfate, and make the solution up to volume, usually 100 cc., with petroleum ether (Figure 5, lower). Determine the concentration of  $\beta$ -carotene by means of photometer (6).

For best results the shaker should operate at 60 to 65 oscillations a minute. The methanol is readily recoverable, and it has been the authors' experience that the redistilled solvent is preferable to the original methanol. Very little

emulsification is encountered when the recovered alcohol is used.

**ALTERNATIVE METHOD OF EXTRACTION (3).** After digestion for 0.5 hour cool the contents of the flask and then pour into a sintered-glass funnel (No. 15180 A, Jena glass, with fritted-glass disks fused in place, Cenco catalog) which is attached to a 0.5-liter suction flask. Apply suction until most of the solvent is removed. Wash the residue on the plate alternately with 25-cc. portions of petroleum ether and absolute alcohol until the filtrate comes through clear. The suction should at no time be applied unless the sediment is partially covered with solvent. After the addition of each wash portion of solvent, more complete

extraction may be obtained by stirring the sediment and solvent on the funnel plate with a stirring rod before applying suction.

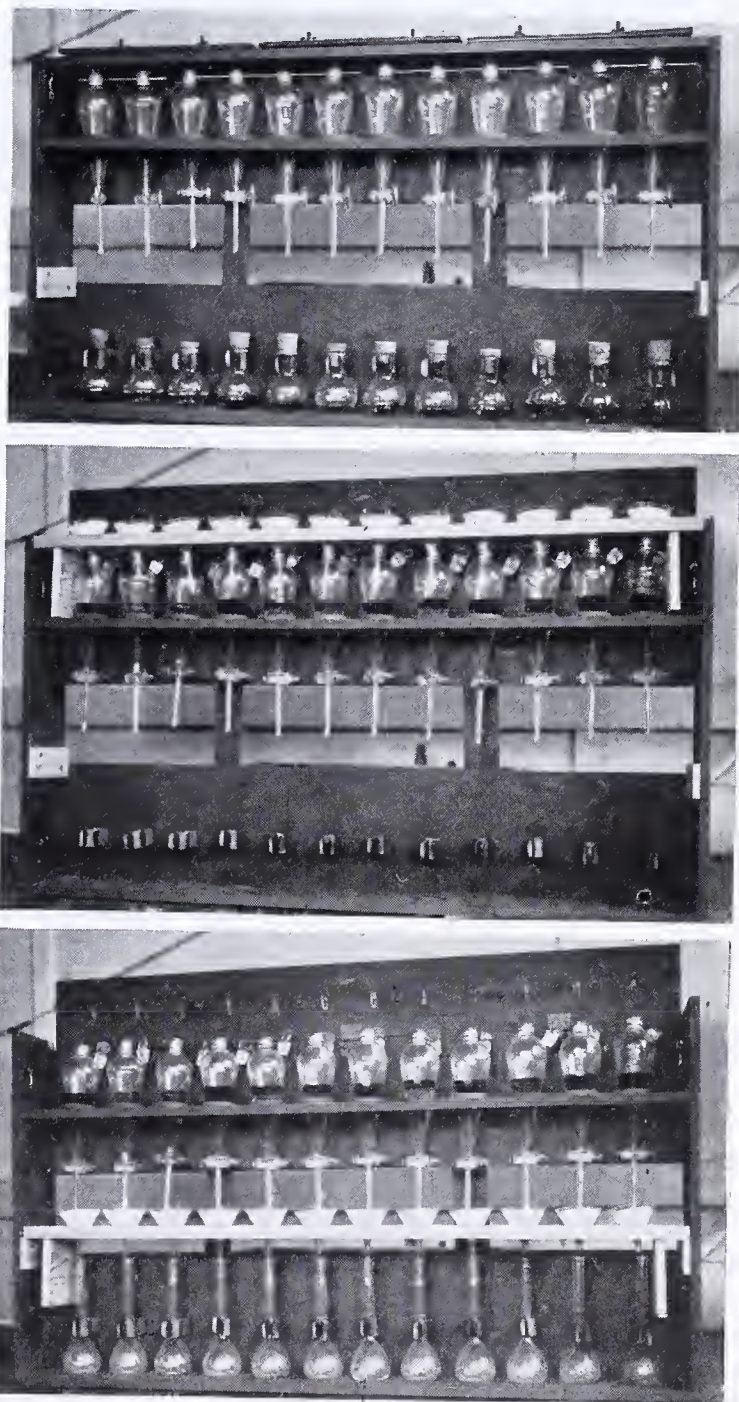


FIGURE 5. RACK WITH FUNNELS AND FLASKS



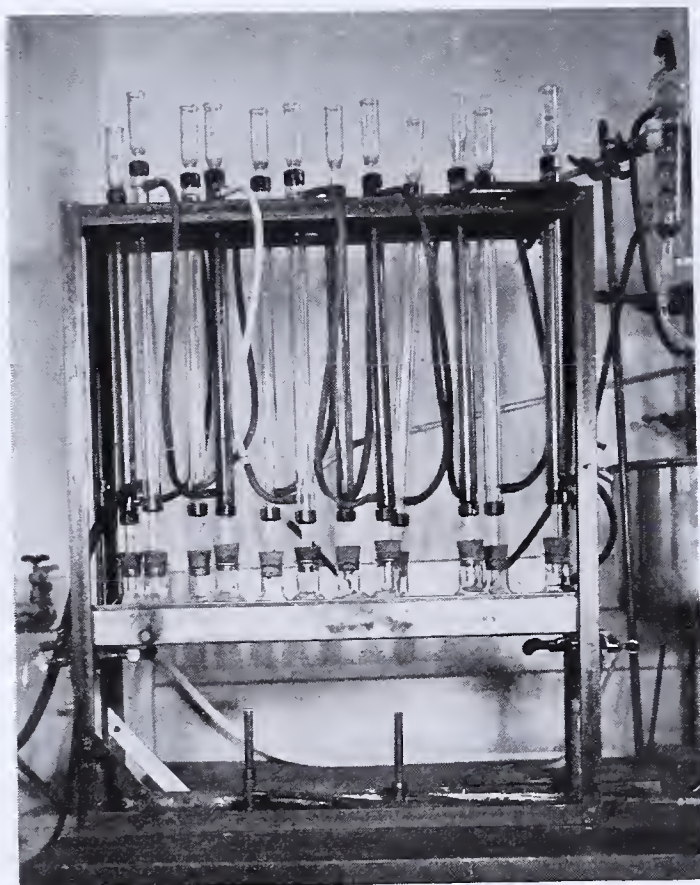


FIGURE 6. FLASKS AND REFLUX CONDENSER

TABLE I. CALIBRATION OF PHOTELOMETER FOR  $\beta$ -CAROTENE DETERMINATION

Concentrations Mg./100 cc.	Reading
0.306	28.0
0.153	51.2
0.102	63.5
0.061	75.8
0.041	83.9

To apply the photelometer to the authors' purpose, a combination of two filters—Cenco lantern blue No. 554, and Noviol A (No. 0.038, 2.95 mm., Corning Glass Works)—was used. This combination cuts out all wave lengths below 400  $m\mu$  and transmits a maximum of 450  $m\mu$ .

The instrument which the authors used in their work was calibrated, using the two filters, by dissolving pure  $\beta$ -carotene crystals in redistilled petroleum ether that had been filtered through anhydrous sodium sulfate to remove traces of moisture, and making the solution up to 1,000 cc. Each cubic centimeter contained 0.0102 mg. of  $\beta$ -carotene. Suitable dilutions were made and readings taken with the photelometer. Table I gives the results.

By plotting the logarithm of the reading against the concentration, a calibration curve was obtained (Figure 7). The curve was then checked colorimetrically, using a dye solution as described by Guilbert (2). The dye was standardized in

three different laboratories against the solution of pure carotene prepared above and found to be equivalent to 0.3191 mg. of  $\beta$ -carotene per 100 cc. Six samples of alfalfa were extracted by the usual procedure, and the carotene content was estimated colorimetrically by comparison with the dye solution. Readings were also taken by means of the photelometer. In Table II the colorimetric values are compared with those secured by means of the photelometer.

The procedure for the determination of  $\beta$ -carotene in alfalfa meals described above has been repeatedly compared with the Peterson and Hughes technique. Table III presents comparative results by the two methods.

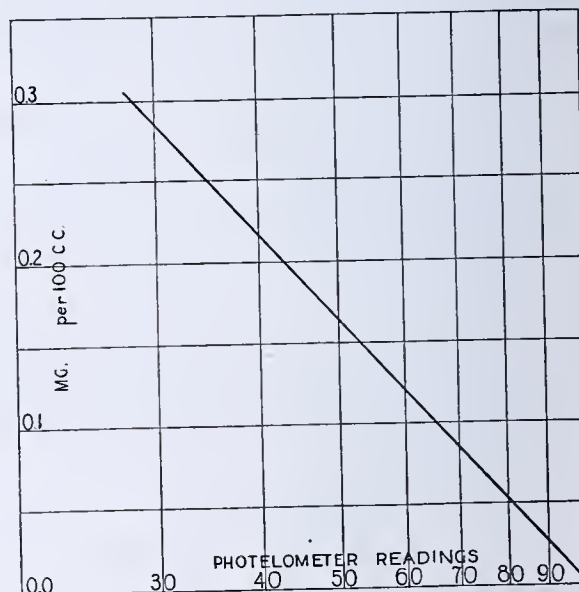
FIGURE 7. CALIBRATION CURVE FOR  $\beta$ -CAROTENE

TABLE III. COMPARISON OF METHODS

Sample	Peterson and Hughes Mg./100 g.	Wirthmore Mg./100 g.
616	12.76	12.76
276	8.51	8.51
305	11.98	12.01
255	7.52	7.65
230	1.64	1.70
175	1.25	1.26
183	9.26	9.29
92	6.76	6.76
3472	24.61	24.12
3473	8.56	8.67

### Summary

The Peterson and Hughes procedure for the determination of  $\beta$ -carotene in alfalfa products has been modified and adapted to the purpose of routine analysis. A convenient shaker greatly facilitates the process of extraction and purification.

The photelometer has been found to be a practical and sufficiently accurate instrument for determining the concentration of  $\beta$ -carotene in petroleum ether extracts from alfalfa meal.

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TABLE II. COMPARISON OF RESULTS BY PHOTELOMETER AND COLORIMETER

Sample	Colorimeter $\beta$ -Carotene Mg./100 cc.	Photelometer
1	0.210	0.210
2	0.130	0.132
3	0.260	0.256
4	0.380	0.365
5	0.100	0.108
6	0.060	0.062



# Determination of Carbon in Organic Compounds

## Modification of the Combustion Vessel

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THE carbon content of a variety of nonvolatile organic compounds can readily be determined by the manometric technique of Van Slyke and Neill (2). The method described involves the use of a combustion vessel, A (Figure 1), adapted from the design of Backlin (1) by Van Slyke, Page, and Kirk (3).

Figure 1. In addition, the arm of the combustion vessel is held rigidly in place by means of a rubber stopper, E, through which it passes, and which fits snugly into the top of D and is kept in position by means of an aluminum plate, F. Screws fasten F to a Bakelite plate, G, attached to the cup of the extraction chamber. Thus the combustion vessel may be easily and rigidly attached to the extraction chamber.

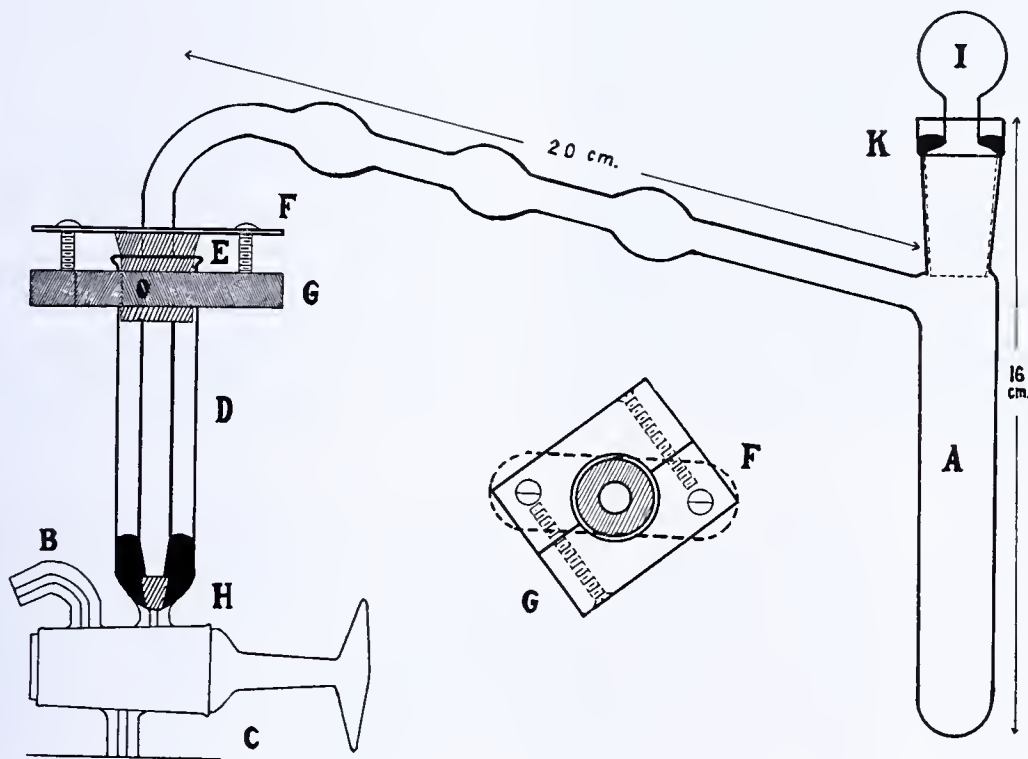


FIGURE 1. MODIFIED COMBUSTION VESSEL FOR CARBON DETERMINATION  
Details of Bakelite attachment, G, to cup are shown in insert, top view

Carbon dioxide-free sodium hydroxide (0.5 M) is admitted into the extraction chamber, C, by means of a soda-lime protected separatory funnel at the cup, D. Upon removal of the separatory funnel the combustion vessel, A, is fitted to the cup as described below. The carbon dioxide liberated by combustion is absorbed by the sodium hydroxide, after which gases other than carbon dioxide are removed under mercury through the side arm, B. The combustion vessel is replaced by a buret and a measured quantity of lactic acid is admitted to the extraction chamber. Carbon dioxide is freed and the pressure at a known volume measured. The carbon dioxide is reabsorbed by strong sodium hydroxide and the pressure measured at the same volume. The pressure of carbon dioxide is secured by the difference between the two readings. A detailed description is given by Van Slyke, Page, and Kirk (3).

Van Slyke *et al.* (3) attach the combustion vessel to B by rubber tubing. With this technique accurate analyses may be obtained, but leaks occur around the rubber tubing with sufficient frequency to invalidate many of the results, and the authors have found it more satisfactory to attach the combustion vessel to the extraction chamber through D. This necessitated a slight change in the design of the arm of the combustion vessel as pictured in

A rubber tip, H, covered by a layer of mercury, prevents gas leaks around the tip of the arm of the combustion vessel. By screwing down the aluminum plate this rubber tip is seated securely in place. As a further precaution the stopper, I, of the combustion vessel is sealed with mercury, K.

The principal advantage of this new design lies in the fact that it removes all possibility of leaks at the point of union between the combustion vessel and the extraction chamber. The method of analysis is identical with that of Van Slyke, Page, and Kirk (3) except that the unabsorbed gas in the extraction chamber is ejected through B under mercury instead of through D.

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# Miniature Penetrometer for Determining the Consistency of Lubricating Greases

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THE accepted method for determining consistencies of lubricating greases is the A. S. T. M. method (1), which, however, requires that a considerable quantity of grease be available—i. e., at least 400 to 500 grams for grease of soft or moderately soft consistencies. Such large quantities of grease are readily obtainable in the manufacturing plants or in storage; however, it frequently happens that information on the consistencies of very small samples of grease is desired. For example, after use on ball or roller bearings, such as the antifriction bearings of motors, automobile wheels, industrial machines, etc., only relatively small quantities of worked or used grease adhere to the bearings. This amount of used grease is inadequate for actual measurements of consistency by the A. S. T. M. method; hence it has been the usual custom to estimate consistency change in use more or less by guess or by comparison with products of known consistency. The accuracy of such practice is, of course, questionable.

Again, in the case of the A. S. T. M. method, it is difficult to obtain accurate check determinations on the same sample if the grease is soft and the penetration of considerable magnitude—for example, 300 and over (units being tenths of a millimeter). The large size of the A. S. T. M. penetrometer cone in relation to the grease surface presented for test, which is limited by the size of the grease container, is responsible for this condition. In taking penetrations of soft greases even in the required size of container, the depth of penetration is such that the original grease surface is considerably disturbed and the bulk of the grease slightly worked. The limited area exposed prevents subsequent determinations on undisturbed surfaces, owing to the danger of the cone's touching the sides of the grease container. The only remaining alternative, therefore, is to smooth out the disarranged surface and again determine the consistency in essentially the same spot. Readings increasingly higher than the original value, since repeated working induces softening, are usually obtained as a result of this procedure.

To circumvent the above objections to the A. S. T. M. method a miniature penetrometer has been designed which may be utilized as an adjunct to the A. S. T. M.

penetrometer and which permits accurate consistency measurements on small samples of greases—that is, about 3 to 5 grams. With a slight modification of the design, consistencies of even smaller samples could be determined. Generally, more than this quantity of used grease can be readily recovered from antifriction bearings of average size. The miniature penetrometer not only permits positive measurements but also allows check determinations with a small supply of sample, and fairly consistent check results are possible on the same sample of used grease. Furthermore, the miniature penetrometer is so constructed as virtually to preclude any possibility of the cone's touching the sides of the special grease container used in this method.

The question of obtaining consistencies of small quantities of semisolid materials such as lubricating greases, as expressed in terms of the depth of penetration of a plunger, has been given study in the past, the apparent solution being to use a small penetrometer needle and a small holder for the grease in place of the present A. S. T. M. grease cone (6.5-cm., 2.56 inches, in diameter) and the rather large-sized grease holder (453.6-gram, 1-pound, tins are recommended).

While various types of small plungers such as glass rods of different weights have been used in earlier work, thereby reducing the size of the plunger cone, the chief difficulty encountered has been in a suitable design of a small holder for the grease, since charging of a small cylinder with a semisolid material such as a lubricating grease causes air entrainment as well as working down of the grease structure and consequent alteration in consistency, usually softening. Both difficulties are overcome by using a split cylinder for the holder. Each half of the cylinder can be charged with grease by simply using a spatula. In this manner, working down of the grease is practically negligible and air entrainment is reduced to a minimum.

With regard to the penetrometer cone, in the A. S. T. M. method the cone, as stated above, has a maximum radius of 6.5 cm. (2.56 inches), the total weight of cone and plunger being 150 grams. In order to take penetrations of small samples it was necessary to reduce the size and weight of the plunger, which was

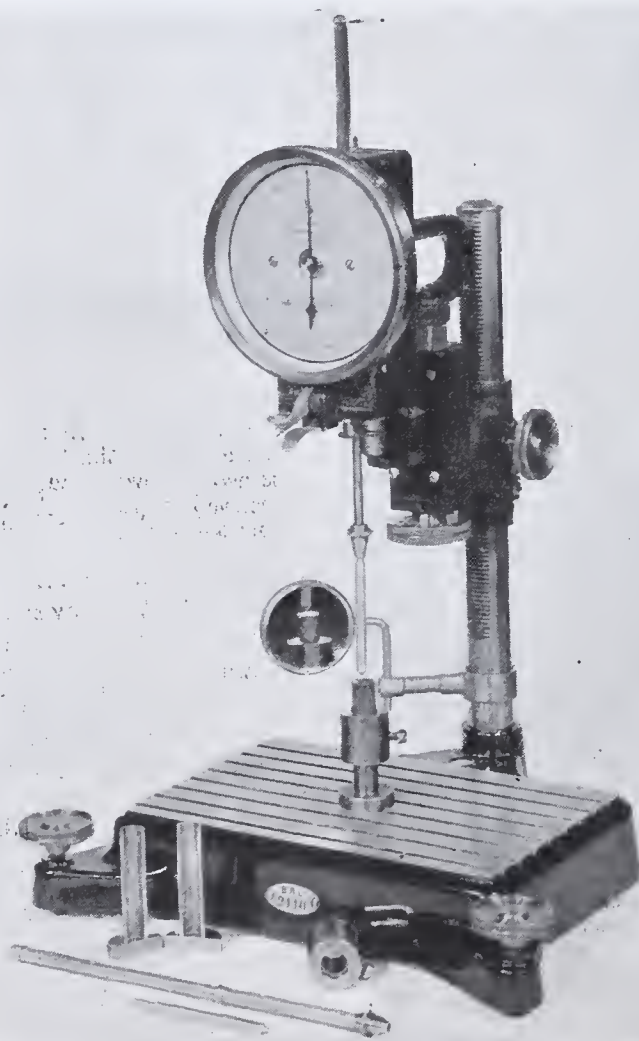


FIGURE 1. MINIATURE PENETROMETER ASSEMBLY



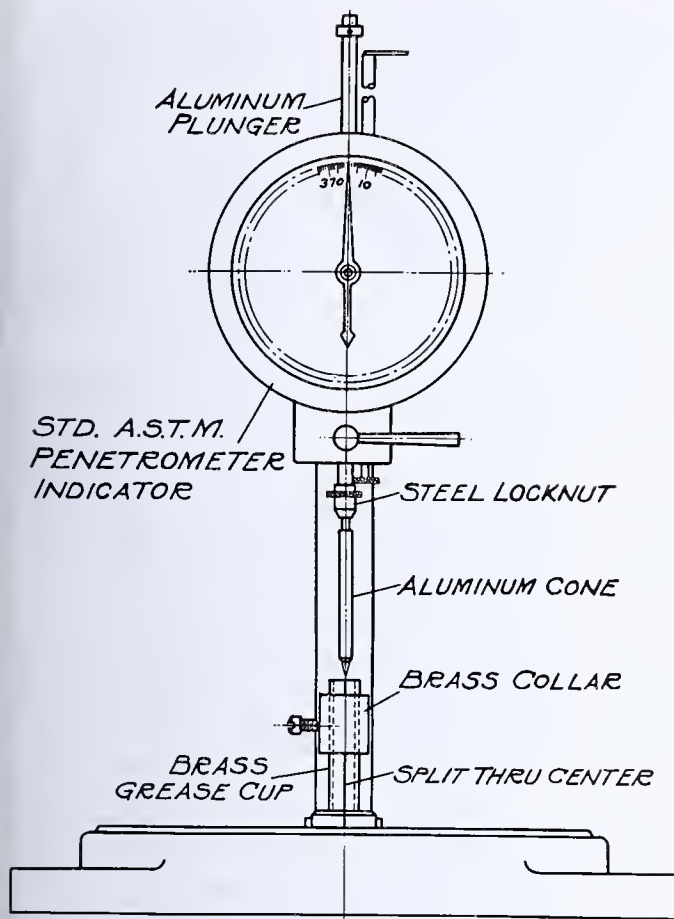


FIGURE 2. DETAILS OF ASSEMBLY

omplished by the use of an aluminum plunger and cone with a total weight of but 20 grams. For very hard greases, provisions are made for adding weights to the grease plunger. The small grease holder and plunger are then used in conjunction with the present A. S. T. M. grease penetrometer indicator, thereby reducing the cost of the miniature penetrometer to a minimum.

### Description of Apparatus

In Figure 1 is shown a photograph of the miniature penetrometer assembled, and in the foreground are shown the individual parts of the grease holder, plunger, and cone. Figures 2 and 3 give details of construction of the grease cup or holder, aluminum plunger, and aluminum cone.

The grease cup (capacity 4 grams of grease) consists of a split brass bushing  $715 \times 0.952$  cm. ( $2.25 \times 0.375$  inches) inside diameter affixed to a suitable base. The penetrometer needle or plunger consists of an aluminum cone which fits into an aluminum plunger and connected to the A. S. T. M. penetrometer indicator. The total weight of the aluminum cone, plunger, etc., is 20 grams. The method of obtaining penetrations follows that outlined in A. S. T. M. Designation D217-33T (1). After bringing the grease to the usual temperature,  $77 \pm 0.556^\circ$  C. ( $77 \pm 1^\circ$  F.), it is

transferred into the small grease holder by means of a spatula, filling each half of the split cylinder. The two halves are then clamped together by means of the brass collar as indicated in Figure 1 and the surface of the grease is smoothed off. In order to ensure centering of the grease holder with the plunger, a centering plate (not shown), with suitable recess to fit the base of the miniature grease holder, is affixed to the base of the A. S. T. M. penetrometer and the grease holder is placed in the recess. This prevents movement of the holder during taking of penetrations. Penetrations are obtained as in the A. S. T. M. method. After each penetration, if check results are desired, additional grease is added to the grease cup, the surface is smoothed off, and the test is repeated. For very hard greases weights can be added to the plunger.

### Experimental Data

In order to determine what relationship, if any, exists between this miniature penetrometer and the A. S. T. M. penetrometer, comparative data were obtained on the most common types of greases of different consistencies, as follows:

- Calcium soap with oil of low and of high viscosity.
- Sodium soap with oil of low and of high viscosity.
- Mixture of sodium and calcium soaps with oil of low and of high viscosity.
- Aluminum soap with oil of low and of high viscosity.

Results obtained are given in Table I. The range of consistencies of the greases shown is that commonly termed in the trade from No. 00 to No. 3, and penetrations have been compared on the worked sample as specified under A. S. T. M. Designation D217-33T (1). As regards reproducibility of results, except for very fibrous greases the miniature penetrometer method compares favorably with the A. S. T. M. method which permits a mean deviation of 3 per cent.

With regard to a possible correlation between the miniature penetrometer and the A. S. T. M. penetrometer, it is seen from

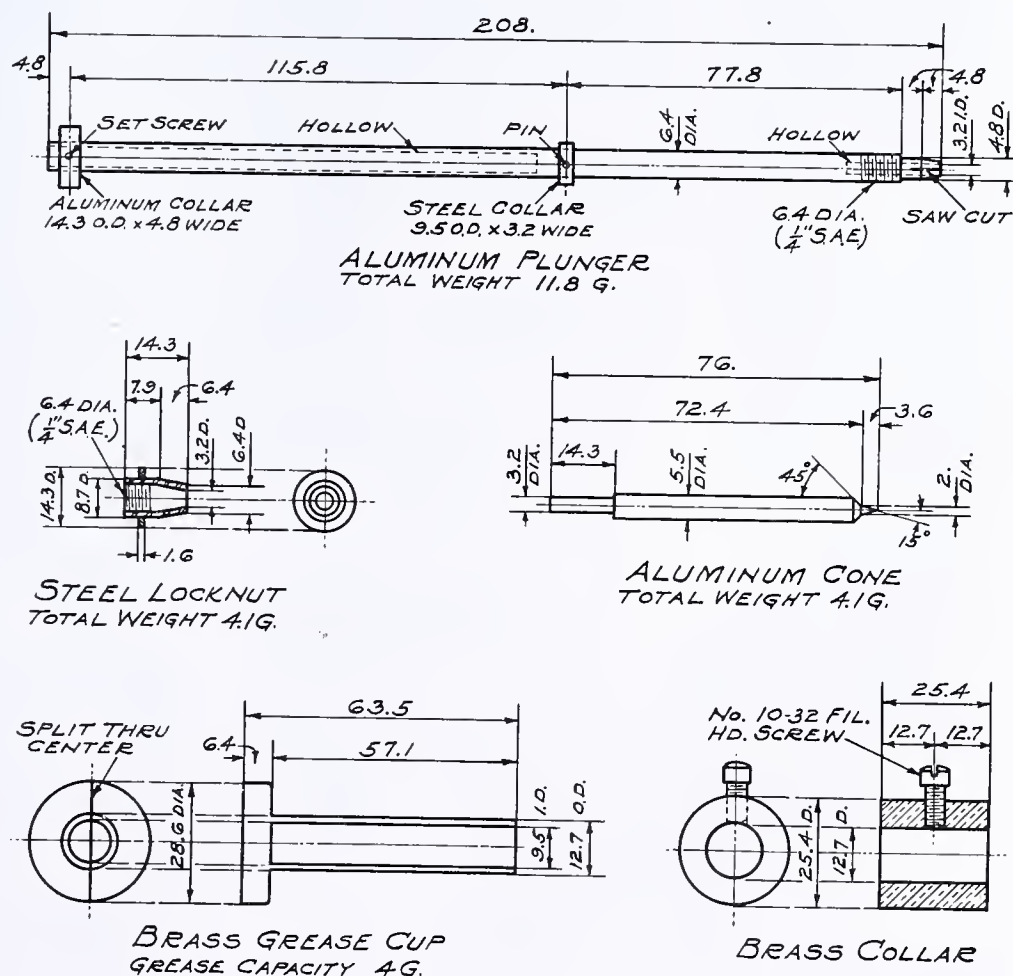


FIGURE 3. DETAILS OF CONSTRUCTION OF GREASE CUP, CONE, AND PLUNGER

All dimensions are in millimeters



the data submitted that the relationship, if any, varies with the texture of the grease, the particular soap used, the viscosity of the mineral oil, etc. In Table II miniature penetrations are shown for greases of different soaps, different textures, and different oils, but having approximately the same A. S. T. M. worked penetration of 300. For an A. S. T. M. worked penetration of about 300 the miniature penetration varies from 120 to 125 for a lime soap or aluminum soap grease of a buttery texture containing a low-viscosity oil to about 170 to 200 for a fibrous soda soap or mixed soda-lime soap grease containing an oil of either high or low viscosity. Apparently, therefore, the fibrous texture of soda soap greases permits greater penetration of the miniature plunger than is the case with the "buttery" textured lime soap cup greases. However, since in studying the performance of lubricating greases in service it is desired to know primarily the relative change in consistency, and since the quantity of grease

TABLE I. COMPARATIVE CONSISTENCY DETERMINATIONS

	(Penetrations of worked samples)					
	Grease A		Grease B		Grease C	
	A.S.T.M.	Miniature	A.S.T.M.	Miniature	A.S.T.M.	Miniature
Buttery texture, calcium soap, mineral oil 300 S. U. at 37.78° C. (100° F.)	327	208	298	111	266	84
	323	209	292	108	262	86
	...	210	...	111	...	84
	...	209	...	110	...	85
	...	211	...	116	...	85
	...	211	...	118	...	...
	...	...	...	116	...	...
Av.	325	210	295	113	264	85
	Grease D		Grease E			
Buttery texture, calcium soap, mineral oil 100 S. U. at 98.89° C. (210° F.)	299	167	278	104	...	...
	295	163	273	103	...	...
	...	166	...	103	...	...
	...	165	...	102	...	...
Av.	297	165	276	103	...	...
	Grease F		Grease G			
Fibrous texture, sodium soap, mineral oil 300 S. U. at 37.78° C. (100° F.)	290	103 <sup>a</sup>	232	57	...	...
	288	110 <sup>a</sup>	225	57	...	...
	287	111 <sup>a</sup>	...	57	...	...
	...	112 <sup>a</sup>	...	62	...	...
	...	...	...	57	...	...
	...	...	...	58	...	...
Av.	288	109 <sup>a</sup>	229	58	...	...
	Grease H		Grease I		Grease J	
Fibrous texture, sodium soap, mineral oil 175 S. U. at 98.89° C. (210° F.)	348	291	286	131	214	60
	341	295	282	126	...	61
	...	298	...	130	...	63
	...	294	...	128	...	...
Av.	345	295	284	129	214	61
	Grease K		Grease L			
Mixed sodium and calcium soaps, mineral oil 200 S. U. at 37.78° C. (100° F.), very short fibers	340	300 <sup>b</sup>	312	177	...	...
	335	288 <sup>b</sup>	316	167	...	...
	...	290 <sup>b</sup>	315	167	...	...
	...	275 <sup>b</sup>	...	177	...	...
	...	288 <sup>b</sup>	...	177	...	...
	...	282 <sup>b</sup>	...	...	...	...
	...	287 <sup>b</sup>	...	...	...	...
	...	278 <sup>b</sup>	...	...	...	...
Av.	338	286 <sup>b</sup>	314	173	...	...
	Grease M		Grease N			
Mixed sodium and calcium soaps, mineral oil 50 S. U. at 98.89° C. (210° F.), very short fibers	296	153	270	110	...	...
	293	155	271	110	...	...
	...	157	...	116	...	...
	...	160	...	111	...	...
	...	155	...	112	...	...
Av.	295	156	271	112	...	...
	Grease O		Grease P			
Buttery texture, aluminum soap, mineral oil 300 S. U. at 37.78° C. (100° F.)	289	125	...	...	...	...
	299	122	...	...	...	...
	...	121	...	...	...	...
	...	122	...	...	...	...
	...	121	...	...	...	...
Av.	294	122	...	...	...	...
	Grease Q		Grease R			
Buttery texture, aluminum soap, mineral oil 100 S. U. at 98.89° C. (210° F.)	340	218	310	173	...	...
	318	220	305	176	...	...
	...	217	...	176	...	...
	...	218	...	175	...	...
Av.	329	218	308	174	...	...

<sup>a</sup> Fibrous texture, difficult to obtain checks.  
<sup>b</sup> Difficult to obtain checks on account of texture.

available is too small for the A. S. T. M. penetrometer, the miniature penetrometer satisfactorily serves the purpose of determining the relative change in consistency of a grease after use compared to the original, unused product. As an example of the application of the miniature penetrometer in practical evaluations, two greases having practically identical A. S. T. M. worked penetrations were used on the same ball bearing operating at 3,450 r.p.m. After such use less than 10 grams of grease were available for examination, insufficient for an A. S. T. M. worked penetration. The consistency of the used grease was therefore determined by the miniature penetrometer and it was found that a considerable difference in consistency of the two greases existed after use, in spite of the fact that the original A. S. T. M. worked penetrations were practically identical. Table III points this out and shows that the A. S. T. M. worked penetration does not necessarily predict the consistency of greases after use in ball bearing.

nor is it necessarily a criterion of leakage tendency.

TABLE II. GREASE CONSISTENCIES

Soap	Texture	Viscosity of Oil	Miniature Penetrations for A.S.T.M. Worked Penetration of 300
Soda	Fibrous	Low	175
		High	170
Mixed soda-lime	Very short fibers	Low	200
		High	160
Aluminum	Buttery	Low	125
		High	170
Lime	Buttery	Low	120
		High	165

TABLE III. GREASE CONSISTENCIES

	Grease R	Grease S
A.S.T.M. worked penetration	323	324
Miniature penetration after working in ball bearing	345	456
Remarks	No leakage past bearing seal	Bad leakage past bearing seal

Summary

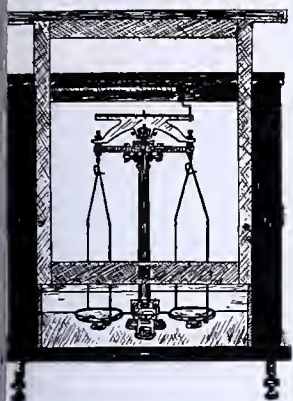
A method of obtaining penetrations of small samples of grease of the order of 4 grams is described, which gives results of reasonable reproducibility. The apparatus is inexpensive, since it utilizes the present A. S. T. M. penetrometer and requires in addition only a simply constructed grease holder and an aluminum plunger and cone. It is a valuable adjunct to the A. S. T. M. penetrometer.

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# Microchemistry

## Microanalysis

SIMULTANEOUSLY with the recent emphasis upon microanalysis and microchemistry in this edition of *INDUSTRIAL AND ENGINEERING CHEMISTRY*, the question arose as to a proper definition which could guide authors, as well as ourselves, in deciding whether a given contribution belonged in that part of each issue devoted to microanalysis. We turned to the officers of the Division of Microchemistry, and through a committee those prominent in the work were solicited for opinions. The result follows and presents the extent of the unanimous agreement on the part of the committee and the divisional officers.

In allocating space for articles, we shall be guided by this definition. It will be noted that authors are expected to express an opinion in cases of possible doubt as to that portion of the *ANALYTICAL EDITION* in which their contribution should appear.

Microanalysis consists of techniques whose primary purpose is the ascertaining of chemical composition where the quantities dealt with are not more than one tenth as large as in customary laboratory practice. Manipulative and observational techniques, which even though nonchemical are peculiar to or especially important to microanalysis, shall be included.

The editor of the journal shall interpret this definition and, guided by the expressed opinions of the author and the reviewer, shall allocate papers to the microchemical or the general section of the journal.

## Microtechnique of Organic Qualitative Analysis

### Classification Reactions of Compounds of Carbon, Hydrogen, and Oxygen

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IN ALL schemes of qualitative organic analysis, the unknown substance is classified as a definite type of compound by the use of classifying reactions. These reactions are usually carried out in a definite order, so that each reaction will identify but one or, at most, two types of compounds. In schemes which use the solubility behavior of organic compounds, the number of classification reactions which must be carried out is considerably reduced. In all other respects, however, the schemes are the same as those which are based on the elementary composition of the substance, such as the scheme of Mulliken and Huntress (17). The next step, therefore, in the development of the microtechnique of qualitative organic analysis, after the preliminary examination and solubility tests described in previous papers (8, 21) is to work out the procedure for the so-called classification reactions for compounds containing carbon, hydrogen, and oxygen. These reactions are the fuchsin test for aldehydes, Molisch test for carbohydrates, titration for acids, ferric chloride and alkali solubility for phenols, saponification for esters, phenylhydrazine test for ketones, and sodium test and solubility test for alcohols. The tests are carried out in that order until a positive test is obtained which places the substance in that group.

The following classification reactions are for compounds containing carbon, hydrogen, and oxygen only. The only

reaction which may be called a real classification test for compounds containing other elements is the titration of nitrogen-containing compounds. This test will be described in a subsequent paper.

#### Fuchsin Test for Aldehydes

Emich (4) mentions this test briefly but leaves the method of applying the test to the reader.

The authors carried out the test in the case of water-soluble substances by placing 2 drops (from a capillary pipet) of the reagent (prepared according to the directions of Mulliken and Huntress, 17) in a shallow depression of a white porcelain spot plate. A tiny drop (0.02 to 0.05 cu. mm.) of the substance is added to the reagent drop, stirring if necessary. A distinct pink, red, or purple color develops within 2 minutes if the substance is an aldehyde. In the case of solids, a tiny crystal is placed in the spot-plate depression. To this is added just enough aldehyde-free alcohol to dissolve it and then the reagent as above. With water-insoluble liquids the authors proceeded as with solids, using 0.02 to 0.05 cu. mm. of the substance.

#### Molisch Test for Carbohydrates

Emich mentions this test also (5) but as Huntress (17) points out, the alcoholic reagent Emich employs as well as his procedure for mixing the reagents may lead to incorrect



conclusions. The authors have therefore taken the method of preparing the reagent which Huntress recommends—that is, a freshly prepared chloroform solution of  $\alpha$ -naphthol. The test is carried out as follows:

End A (Figure 1, *a*) of the capillary (1-mm. bore, 100-mm. length) is dipped into the 1 per cent sugar solution until a droplet about 0.5 cm. long has risen in the capillary. If too much is taken, the excess can be removed by inserting the point of a triangular piece of filter paper into this end of the capillary (Figure 1, *b*). The capillary is then inclined towards B and the droplet allowed to flow a short distance towards the middle of the tube. The finger is then placed over end B and end A dipped into the reagent solution (a drop on the slide will do, Figure 1, *c*). When the pressure of the finger is gradually released, the reagent (1 to 2 mm.) rises in the tube. Both droplets are then allowed to slide to the middle of the capillary. End A is then closed with the finger and end B dipped into concentrated sulfuric acid to a depth of 1 cm. The finger is then removed from end A, the acid enters the tube for a distance of 1 cm., and the end is closed again with the finger. All the droplets are then allowed to slide to the middle of the capillary (Figure 1, *d*). End B is wiped off and sealed in the flame. All droplets are then centrifuged briefly (1 or 2 turns) to end B. This brings the sulfuric acid on the bottom, followed by the reagent, and then the test solution. Thus mixing of the reagent and sugar solution is accomplished but the proper contact between acid layer and reagent-substance layer is secured. In the presence of carbohydrates, a red ring forms at the acid-reagent interface. Then the solutions are mixed by means of a glass thread, whereupon a violet color appears throughout the liquid. On dilution a violet precipitate may appear. The sealed end is then cut off and the liquid blown out into a depression of a spot plate. Excess concentrated ammonia is added. A yellow-red color results.

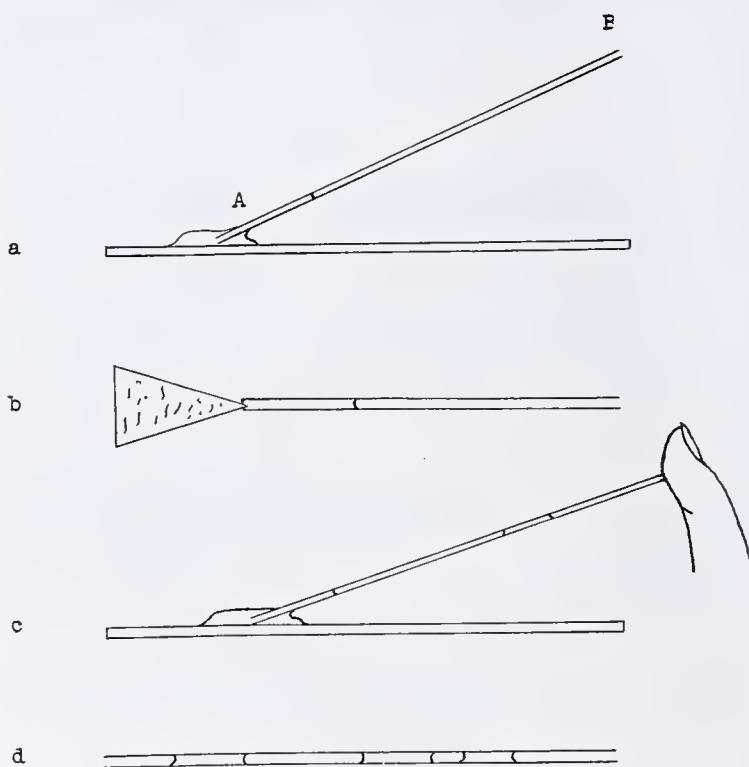


FIGURE 1. CARBOHYDRATE TEST

Ten carbohydrates were tested in this way and correct results obtained in each case.

### Titration of Acids

The titration of a few milligrams of acids has been described by a number of authors (3, 9, 18). Since, however, according to Mulliken and Huntress, it is necessary to proceed with the titration under certain very definite conditions in order to classify the substance properly as an acid and to avoid the possibility of including phenols, esters, anhydrides, or lactones in this group, it was necessary to reproduce these conditions as nearly as possible on a micro scale. At the

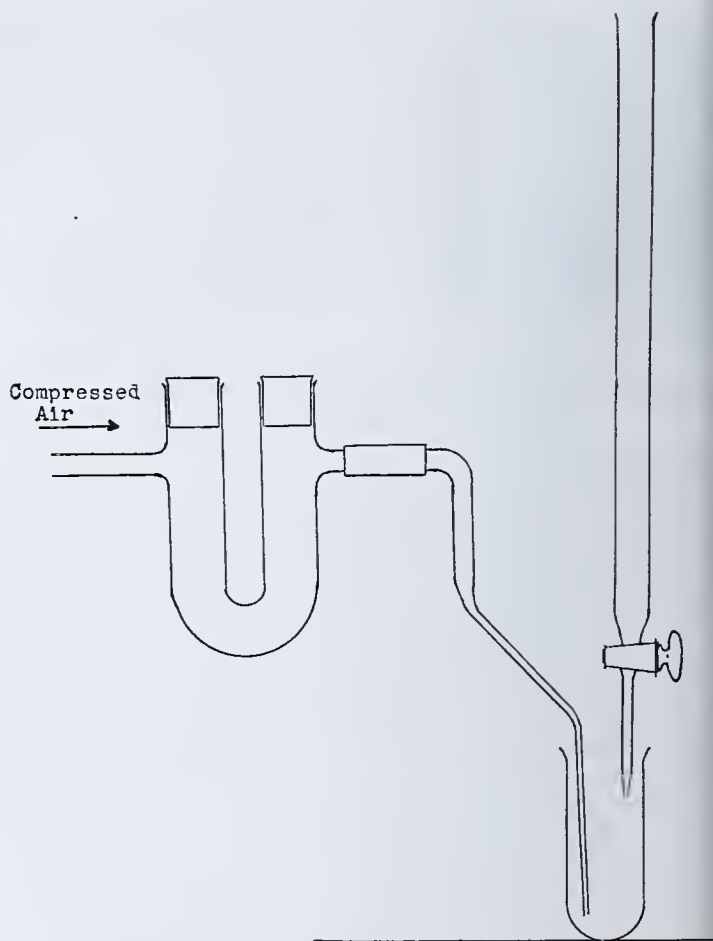


FIGURE 2. APPARATUS FOR TITRATION OF ACIDS

same time the comparatively elaborate equipment and procedure used in the ordinary quantitative microtitration should be avoided, in order to adhere to one of the principles of the authors' work—that is, to keep the apparatus as simple as possible.

The sample, if a solid, is weighed out either on a Salvior balance or a good analytical balance. About 5 mg. are taken. In the case of liquids the density of which is known, a definite volume can be taken in a capillary. The sample is dissolved in 2 ml. of water in a 7- to 10-ml. microbeaker made from the bottom of a test tube. One drop of phenolphthalein indicator solution is added. A fine capillary connected to a source of compressed air through a soda-lime tube is dipped in the solution (Figure 2). It is placed to one side so that the rising stream of bubbles causes thorough circulation. The carbon dioxide-free air forms a cover over the liquid surface and prevents the absorption of carbon dioxide from the atmosphere. The tip of a 10 ml. buret (in 0.05 ml.) is dipped into the beaker (but not into the solution) opposite the air inlet capillary. The 0.02 N sodium hydroxide is added dropwise at such a rate that the color due to one drop is dissipated before the next drop is added. The end point is reached when the color persists for more than 1 minute. In the case of water-insoluble substances, 2 ml. of alcohol are used in place of the water as solvent.

According to Huntress (17), a substance is considered an acid if it gives a sharp end point (one drop of alkali causing a permanent color change) and a normal color change (faint pink). A series of titrations on water-soluble and insoluble substances showed that the conditions described are satisfied by the microprocedure.

### Ferric Chloride Test for Phenols

Emich (6) mentions this test but gives no details for carrying it out. He lists the colors obtained with some phenols (see also Meyer, 15). Kissler and Kondo (14) describe a spot-test procedure which, however, is limited in its application. The authors used a spot plate and the reagent d



scribed by Mulliken and Huntress. The droplet of reagent used should be small. The characteristic color changes can readily be observed.

According to Mulliken and Huntress, if no color is obtained in the above test in the case of solids, a test of the solubility first in water and then in 5 per cent sodium hydroxide must be applied. This test can be carried out by the solubility testing procedure described in a previous paper (21).

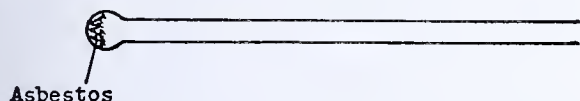


FIGURE 3. DISTILLATION TUBE

If the substance is found to be soluble in water in the cold and to give no color with ferric chloride, it is not a phenol. If it is soluble in five per cent sodium hydroxide it should be regarded as a member of this group.

### Saponification of Esters

The saponification procedures described in the microchemical literature are almost exclusively restricted to heavy fats and oils (12, 16, 20). While there was no doubt that the usual saponification methods using alcoholic alkali could be readily adapted to microwork, the authors were so impressed by the advantages of the method of Redeman and Lucas (19), using a diethylene glycol solution of the alkali, that they determined to develop a microprocedure based upon it. Again they found that despite the apparent simplicity of the macroprocedure, the micromethod was still simpler.

A distillation tube is prepared by blowing a bulb about 6 to 7 mm. in diameter at the end of a Pyrex tube of 4- to 5-mm. bore and about 100 mm. long (Figure 3). This bulb is half filled with ignited asbestos and 30 cu. mm. of the diethylene glycol solution made up as described by Redeman and Lucas are introduced directly into the bulb by means of a capillary pipet. Then 10 cu. mm. of the ester are introduced in the same way. Care should be taken that no liquid touches any part of the walls of the tube except the bulb. The capillary pipet should be wiped off on the outside before it is introduced into the distillation tube. If the liquids do not soak into the asbestos, brief centrifuging will bring this about.

The tube is then placed in a Benedetti-Pichler heating block (2), and the block and tube are heated slowly until a condensate appears at the portion of the tube projecting from the block. The rate of heating can then be increased until a definite ring of condensate forms. Redeman and Lucas have determined the reaction times of various esters and found that all reactions, when carried out on a large scale, are complete within 2 minutes; hence, by the time the first condensate appears the reaction is complete. After formation of the ring of condensate, heating is continued until the ring is about 1 or 2 cm. from the block. It is then taken up in a capillary pipet. Sometimes no definite ring forms, only a larger number of drops. These can be gathered together and picked up by the capillary pipet just as readily.

Since there is always water in the reagents even if it is not added in making up the alkali, some water will distill with the alcohol. In the case of water-insoluble alcohols this is not serious, since the combined water and alcohol condensate in the capillary pipet can be separated into its components by sealing the fine end of the pipet and centrifuging. The capillary is cut at the interface and the alcohol transferred to a boiling point tube. In the case of water-soluble alcohols, some help is obtained from the fact that these boil at temperatures below the boiling point of water. Thus the first condensate is the alcohol, which, with care, can be collected without the water. In any event the alcohol is dried as described by Benedetti-Pichler (11). The boiling point can then be determined as described by Emich (7) and the alcohol thus identified. The acid part of the ester is identified by adding a drop of water and a drop of alcohol to the residue from the distillation. After stirring and centrifuging, the liquid is transferred to a centrifuge cone by means of a capillary pipet. A drop of phenolphthalein is added and the solution acidified with sulfuric acid. Centrifuging removes the potassium sulfate and the clear liquid can be siphoned off and analyzed for the acid, as will be described in a subsequent paper.

### Acid Anhydrides and Lactones

There is no classification reaction for these compounds, but if the saponification equivalent is less than 500 and no alcohol is obtained in the foregoing test the compound is placed in this group.

### Phenylhydrazine Test for Ketones

Procedures for carrying out this test have been described by Behrens (1), Emich (4), and Garner (10). Garner uses up to 50 mg. in a "microflask" or "anilide tube"; the others employ microscope slides. Griebel and Weiss (13) describe a technique which is limited to easily volatile substances. The authors carried out the test in capillary tubes. They claim no advantages for their method except that it makes it possible to recover the product more readily for further identification. About 0.5 cu. mm. of reagent is drawn into a capillary tube (1-mm. bore) and allowed to slide to the middle.

About 5 times as much of the sample is drawn in at the other end of the capillary. The first end is sealed and the reagent and sample are centrifuged to this end. An immediate precipitate is obtained with ketones.

### Alcohol Test with Sodium

Mulliken and Huntress place a compound in this group if it has failed to give a positive reaction in the preceding tests and if it is soluble in 50 parts or less of water at 20° C. (see also 21).

If the substance does not dissolve in 50 parts of water at 20° C. the sodium test is applied.

The reagent is prepared by melting some sodium in a hard-glass test tube. A glass tube is drawn out into a thin-walled capillary of about 0.5-mm. bore and about 150 mm. long. Without cutting the capillary from the wide tube, the former is dipped into the molten sodium and suction cautiously applied (Figure 4). The sodium will rise in the tube and is then allowed to cool and congeal. Short pieces of the filled capillary are used and are cut off just before use to ensure a clean surface of the sodium.

The test is carried out by placing a drop of the alcohol on a slide. A piece of the sodium capillary is laid on the slide so that the fresh-cut end is in the center of the drop. The whole setup is

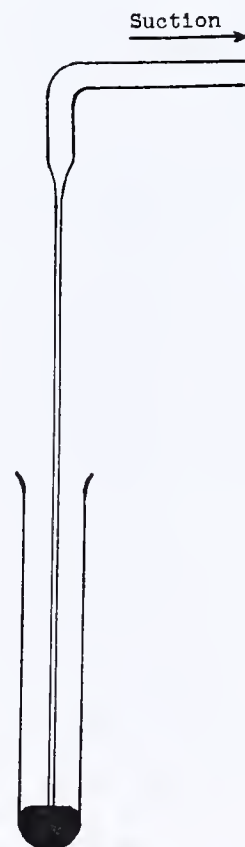


FIGURE 4

placed under a lens or low-power microscope. If the substance is an alcohol, bubbles of hydrogen will appear issuing from the capillary.

### Hydrocarbons and Ethers

If the substance does not give a positive result in any of the preceding tests, it is placed in the group of ethers and hydrocarbons.

### Acknowledgment

The authors wish to express their thanks and appreciation to E. H. Huntress of the Massachusetts Institute of Technology for his kindness in placing at their disposal material which he has not published as yet and for a copy of his unpublished revision of Mulliken's book on qualitative organic analysis.

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# Determination of Ethylene

## In the Internal Atmosphere of Plant Tissues

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DURING certain physiological investigations relating to the handling and storage of apples and pears, a need developed for an accurate chemical method of determining the small amounts of ethylene contained within the fruit tissues. Since these fruits produce ethylene (5, 7), which is definitely known to affect certain chemical changes (6, 8)

that are associated with the ripening and storage of fruit, a means of obtaining data of this nature is desirable.

Although ethylene has been identified as a constituent of fruit emanations (5, 11) and has been semiquantitatively estimated, the procedures used would not lend themselves to the development of a rapid and accurate method for the de-

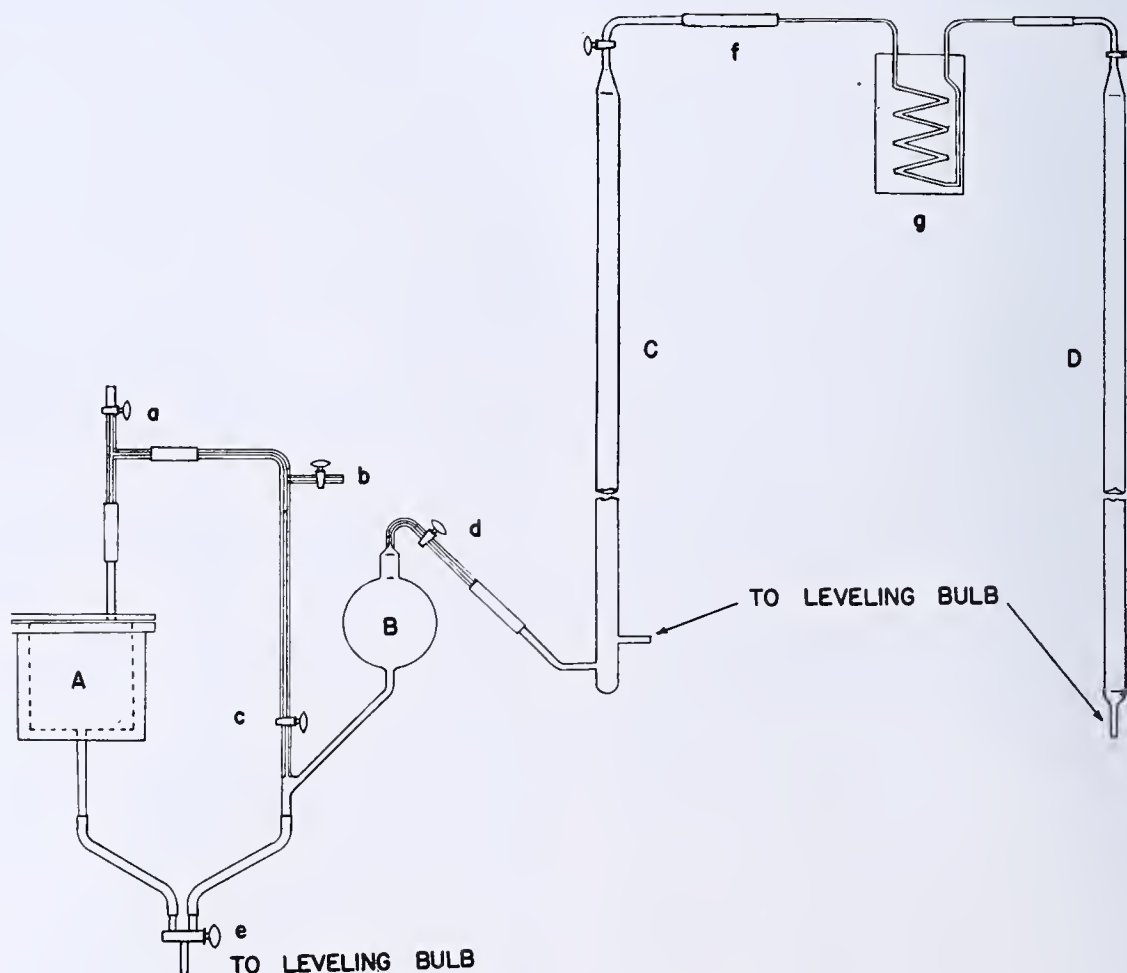


FIGURE 1. DIAGRAM OF APPARATUS



termination of the gas contained in the internal atmosphere of the tissue.

The amount of ethylene that occurs in plant tissues is thought to be very small (4). Nelson (10) reports the ethylene content of McIntosh apples as 0.12 mg. per kilogram. Since 1 kg. of fruit tissue will contain on the average from 300 to 600 ml. of total gas, this represents a dilution in the order of one part in four thousand. If these values are approximately correct, it would appear that a method which could accurately determine 0.001 ml. of ethylene in a dilution of 40 ml. (1 part in 40,000) might suitably serve for the estimation of this gas in the internal atmosphere of fruit tissue.

A survey of the possible chemical reactions which might serve as a basis for a microdetermination indicated that bromination or oxidation with potassium permanganate would be the most promising. A method using permanganate has recently been described by Nelson (10).

Extensive preliminary experiments conducted in this laboratory indicate that the reaction of ethylene with permanganate, besides being affected by traces of acids, bases, or organic impurities, does not always proceed to a definite quantitative product—viz., glycol—and as a result only the roughest of approximations may be attained by its use.

Bromination on the other hand has the distinct advantage that the reaction does not proceed readily beyond the formation of ethylene dibromide and is not so easily influenced by small amounts of foreign materials. For these reasons a simple method modified from the macrodetermination of Davis, Crandall, and Higbee (3) was adopted.

Apparatus

The apparatus consists of three units: an extractor, a purification train, and a reaction flask.

**EXTRACTOR.** The extractor (Figure 1) was constructed on the same principle as a Töpler pump and consisted of two parts: a chamber, *A*, and a pump, *B*. The extraction chamber, *A*, was constructed from an iron pipe 8.9 cm. (3.5 inches) in inside diameter and 7.6 cm. (3 inches) over-all. To the bottom was welded a steel plate fitted with a 0.64-cm. (0.25-inch) steel tube which served as an inlet for the confining fluid. A 1.25-cm. (0.5-inch) iron collar was welded to the opposite end and then carefully machined to give a smooth surface. The cover, equipped with an exit tube, was made from a 0.64-cm. (0.25-inch) steel plate carefully polished and fitted to the collar. A tight connection capable of maintaining vacuum was obtained by the use of a greased rubber gasket. The cover was held in position by means of a heavy screw clamp like those used on specimen jars.

The pumping compartment, *B*, was constructed from a 250-ml. Pyrex bulb and was connected to the extraction chamber with 1-mm. capillary tubing. Stopcock *c* was used to control the flow of gas between these two units. Stopcock *a* provided a means of releasing the vacuum, while *b* led to a manometer for measuring the pressure in the extraction chamber. In order to ensure flexibility a rubber connection was placed between stopcocks *a* and *b*. By means of stopcock *e*, the same leveling bulb was used for forcing mercury into either *A* or *B*.

A nitrometer, *C*, which served to trap the extracted gases, was connected to *B* through stopcock *d*.

**PURIFICATION.** The purification unit consisting of a small Desiccchlore tube, *f*, and a copper coil, *g* (2 mm. in inside diameter  $\times$  100 cm.), immersed in a solid carbon dioxide-ether mixture, was connected between nitrometer *C* and gas buret *D*. The total volume of the tube and coil was 5.3 ml. Buret *D*, equipped with a leveling bulb containing mercury, served to store and measure the purified gas prior to analysis.

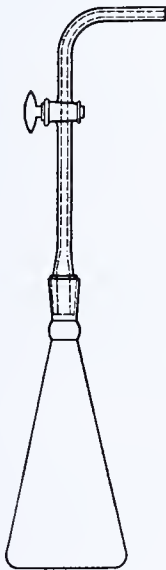


FIGURE 2

TABLE I. RECOVERY OF ETHYLENE ADDED TO APPLE TISSUE

Ethylene Taken Ml.	Ethylene Recovered Ml.
0.058	0.051
0.057	0.059
0.058	0.056
0.058	0.062
0.061	0.061

**REACTION FLASK.** The reaction flask (Figure 2) was constructed from a 50-ml. Erlenmeyer to which was sealed a <sup>12</sup>/<sub>30</sub> standard taper and a capillary stopcock.

Operation

A weighed amount of tissue (either whole or cut) was placed in chamber *A*. The cover was then clamped in position and connected to the pumping compartment. With stopcock *a* open *A* was filled with mercury from the leveling bulb; *a* was then closed and the mercury allowed to drain away, leaving the tissue in a Torricellian vacuum. By means of stopcock *e* and the same leveling bulb, chamber *B* in turn was filled with mercury and evacuated. Nitrometer *C* was then filled with mercury, over which was placed 1 ml. of 2.5 per cent ammonium hydroxide solution.

The gas in the storage flask was now completely removed and transferred to nitrometer *C* by merely raising and lowering the leveling bulb and operating stopcocks *c* and *d*. This process was continued until no further gas could be extracted.

After standing for 15 minutes in nitrometer *C*, the gas was passed slowly (approximately 4 ml. per minute) through the purification train to the measuring buret, *D*, where it remained until removed for analysis.

The reaction flask (Figure 2) was then charged with 5.00 ml. of 0.0025 *N* potassium bromate (measured with a microburet) and 0.5 ml. of 6 *N* sulfuric acid, and then partially evacuated. Buret *D* was detached and approximately 40 ml. of sample were transferred to the reaction flask. One milliliter of 0.1 *N* potassium bromide was finally introduced without releasing all the vacuum. This mixture was shaken vigorously for 15 minutes on a mechanical shaker and then 1 ml. of 0.1 *N* potassium iodide was introduced by means of the residual vacuum. The iodine liberated was titrated with 0.0025 *N* sodium thiosulfate from a microburet. The amount of potassium bromate used for bromination was determined by the difference between the blank run (using air) and the actual determination. Duplicate blank runs checked consistently within 0.02 ml. One-tenth milliliter of 0.0025 *N* potassium bromate is equivalent to 0.0028 ml. of ethylene at normal temperature and pressure.

In all determinations a correction was made for the gases remaining in the purification train.

Discussion and Results

**EFFICIENCY OF EXTRACTION.** To determine the efficiency of the apparatus for extracting ethylene from fruit tissue, blank determinations were made using ethylene-air mixtures. Approximately 100 grams of sliced apple were placed in the storage compartment and all the free ethylene present was removed by extraction. Small known quantities of ethylene were introduced into the chamber and sufficient time was allowed to ensure diffusion throughout the fruit and container. Forty milliliters of air were then introduced (that amount being the approximate volume of gas taken for analysis). This gaseous mixture was then removed and analyzed in the manner previously described.

From the results of a number of determinations, shown in Table I, it is apparent that small quantities of ethylene can be recovered quantitatively when added to apple tissue. Furthermore, consecutive tests on fresh samples have failed to show any trace of ethylene after the first extraction. Ethylene did not appear to be given off in a definite pressure range.

The advantages of this type of extraction are: It attains a practically complete removal of gas; it permits the study of either whole or cut tissue; and it is equipped to measure the



TABLE II. MICRODETERMINATION OF ETHYLENE

Ethylene Taken Ml.	Ethylene Found Ml.
0.0026	0.0025
0.006	0.006
0.011	0.011
0.029	0.028
0.052	0.049
0.066	0.066
0.063	0.061

TABLE III. ETHYLENE CONTENT OF INTERNAL ATMOSPHERE OF FRUIT AND VEGETABLE TISSUES

Kind of Fruit	Method of Sampling	Ethylene Found Ml./100 g.
Apple: Gravenstein	Longitudinal sectors	0.019
		0.016 <sup>a</sup>
	Whole apple	0.026
		0.040
		0.063
		0.039
Red June	Average of 6 whole fruits	0.022
	Longitudinal sectors	0.038
	Average of 6 whole fruits	0.008
Bartlett Pear	Whole fruit	0.012
		0.015
		0.029
		0.010
		0.008
		0.020
Peaches: Hale	Whole fruit	0.012
Crawford		0.010
Tomatoes	Whole fruit	0.006
Cantaloupe	Gas from cavity	0.002
	Longitudinal sectors	<0.001
Potatoes	Long sectors	<0.001
Bananas	Long sectors	<0.001

<sup>a</sup> Sectors taken from same apples 3 hours later.

pressures at which the gases are extracted. Although several methods (1, 2, 9, 10) for the removal of internal gases from fruit tissue are described in the literature, none attained all these objectives.

EFFECTIVENESS OF PURIFICATION TRAIN. In order to determine the ethylene content in the vapors derived from fruit tissues it was necessary to remove the other components, such as aldehydes, esters, and alcohols.

Preliminary experiments carried out under the conditions specified for analysis showed (1) no bromination of ethyl acetate, (2) slight bromination of ethyl alcohol, and (3) considerable bromination of acetaldehyde.

To eliminate these substances, 1 ml. of 2.5 per cent ammonium hydroxide was placed in nitrometer C over which the vapors were permitted to stand for 15 minutes. Blank determinations showed that this treatment completely removed both acetaldehyde and alcohol vapors, even when present in great excess over that found in fruit vapors. In using this procedure, however, care must be taken to prevent any of the ammonia from entering the analytical flask, since it would alter the acidity of the reaction mixture. To ensure the removal of ammonia and possibly other active agents, the extracted gas was finally passed through a Desiccchlor tube and a cold trap.

Since it appears that ethylene is the only unsaturated gas present in apple (5), pear (7), and banana (11) vapors, no special precautions were taken to remove possible traces of acetylene or propylene.

ACCURACY OF THE ANALYTICAL METHOD. To determine the accuracy of the analytical procedure, a number of typical runs were made with pure ethylene and are tabulated in Table II.

ETHYLENE CONTENT OF THE INTERNAL ATMOSPHERE OF PLANT TISSUE. Using the procedure outlined, the ethylene content of various kinds of ripe fruit material was deter-

mined. In some of these analyses, gas samples were taken from whole fruits; in others, from slices of eight or more selected specimens. In the case of the cantaloupe, the gas sample from the cavity was taken by inserting a glass tube and extracting the gas directly into the buret. The results are tabulated in Table III.

Table III shows that there is considerable variation in the ethylene content of individual fruits taken from the same lot. Ripe Gravenstein apples showed a variation of 0.022 to 0.063 ml. per 100 grams of tissue. Bartlett pears showed a variation of from 0.008 to 0.029 ml. Some of the data indicate that gas samples taken from whole fruits gave higher ethylene values than similar samples taken from cut fruit. Whether this difference is due to loss of gas in cutting or to variation in the ethylene content in different parts of the fruit is not known at the present time. It is apparent, however, that some gas is lost from cut tissue, since more ethylene was found in cut Gravenstein tissue analyzed immediately after sampling than in similar tissue analyzed 3 hours later.

There is considerable variation in the amount of ethylene found in different kinds of fruits and vegetables. Since the ethylene content of a given variety of fruit is dependent on a number of factors, these values are merely indicative of its presence. The variation in each type of material is a study in itself, and beyond the scope of this paper.

## Summary

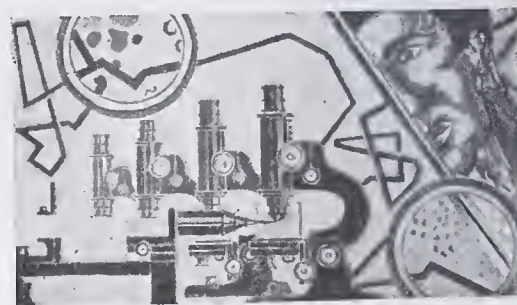
A bromination micromethod for the accurate determination of ethylene within a range of 0.001 to 0.06 ml. at normal temperature and pressure in a volume of 35 to 40 ml. has been developed, and a new apparatus devised for the complete removal of internal gases from plant tissue.

A number of analyses have been carried out to show the presence of unsaturates (ethylene) in various kinds of tissue in quantities measurable by this method.

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# Qualitative Separations on a Micro Scale

## Separations in the Alkaline Earth Group

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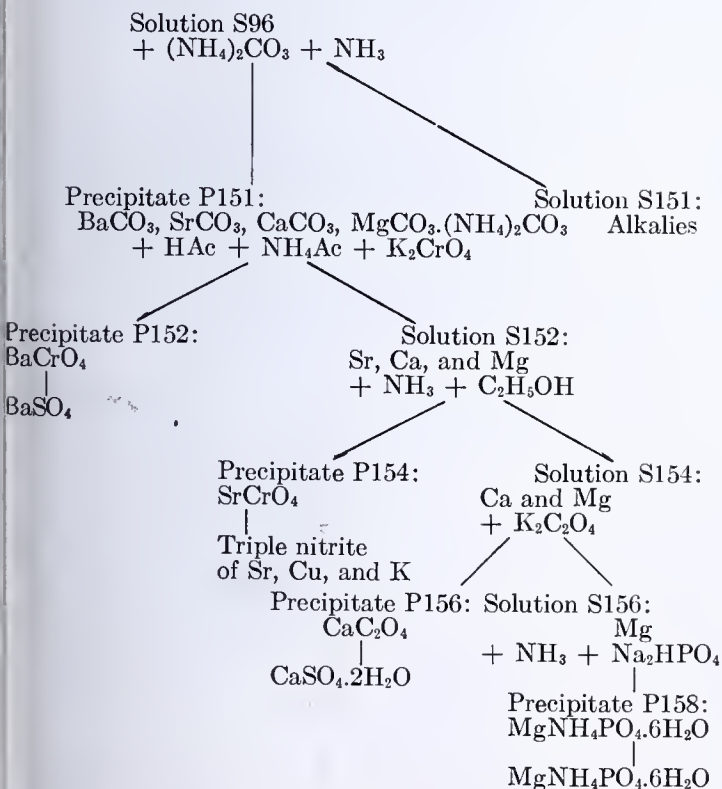
Washington Square College, New York University, New York, N. Y., and University of California at Los Angeles, Calif.

The procedure of Noyes and Bray for the separation and analysis of the alkaline earth group has been applied on a micro scale. The quantities of the reagents have been chosen so as to permit the analysis of 1.2 mg. of nonmetallic materials or 0.6 mg. of metals and alloys. The perchlorate ion, introduced by the use of perchloric acid as solvent, is removed before precipitation of the alkaline earth group.

THE present paper deals with the elements commonly included in the alkaline earth group which consists of barium, strontium, calcium, and magnesium. The methods follow the scheme of Noyes and Bray (5) with the exceptions of the confirmatory tests for barium and strontium. The working technique and apparatus are essentially the same as those suggested for the separations of members of the third analytical group (3). To facilitate the precipitation of the whole group as carbonates, of strontium chromate, and of magnesium ammonium phosphate the use of the vibrating armature of an ordinary door bell was found to be effective.

The tabular outline shows the general scheme for the separations. The numbers of the precipitates and solutions correspond to the numbers of the paragraphs in Noyes and Bray (5) in which the analogous macroprocedures are described.

### Procedure



**PRECIPITATION OF THE ALKALINE EARTH GROUP.** In order to remove perchlorate ion and the large quantity of ammonium salts, evaporate ammonium sulfide filtrate S96 to dryness in small portions in a cone over a steam bath. Evaporate twice with 25-cu. mm. portions of concentrated hydrochloric acid.

Extract the residue with three 50-cu. mm. portions of water, separating any insoluble residue by centrifuging after each addition and evaporate the combined extracts over steam in small portions in a platinum crucible. Moisten the residue with 10 cu. mm. of 6 *M* ammonium chloride solution and evaporate to dryness. Heat the crucible at 140° C. for 10 minutes. Then place the crucible on a silica triangle and heat cautiously with a small flame until fumes are no longer given off. Finally heat the crucible just to the point of dull redness and discontinue further heating. Extract the residue with several 10-cu. mm. portions of water, add the solution to a cone, evaporate to dryness, and dissolve in 10 cu. mm. of water. The solution should be clear at this point. If it is not, separate solution and residue by centrifuging.

To the solution add 15 cu. mm. of ammonium carbonate reagent (5) and 15 cu. mm. of 95 per cent ethyl alcohol. If the precipitate is large, add 15 cu. mm. more of each of these solutions. Stir with a glass thread, attach to the vibrator, shake intermittently for 10 minutes, and centrifuge. Remove the solution and wash the precipitate with a little ammonium carbonate reagent.

**PRECIPITATION OF BARIUM.** Add to precipitate P151 in the cone 5 to 15 cu. mm. of 6 *M* acetic acid and warm on the steam bath until the carbonates are dissolved. Evaporate the acetic acid solution to dryness over the steam bath in a current of air. To the residue add 10 cu. mm. of water, 10 cu. mm. of 3 *M* ammonium acetate, and 2 cu. mm. of 6 *M* acetic acid. Heat the mixture on the steam bath and add to it, in portions of about 0.3 cu. mm., 3 cu. mm. of 1.5 *M* potassium chromate, shaking after each addition. If the precipitate is large, add 2 cu. mm. more of the potassium chromate solution. Allow to stand on the steam bath for 5 minutes. A yellow precipitate shows the presence of barium. Centrifuge and separate solution and precipitate. Wash the precipitate with a little water and set it aside for later use.

Estimate the amount of barium present by comparing the size of the precipitate with a known amount of barium chromate precipitate obtained by treating a solution of barium nitrate in the same manner as the unknown solution.

**PRECIPITATION OF STRONTIUM.** To solution S152 which may contain strontium, calcium, and magnesium add 6 *M* ammonia until the solution turns yellow and then 5 cu. mm. more. Heat in a water bath to 60° to 70° C. and add in three portions 15 cu. mm. of ethyl alcohol, shaking or stirring after each addition if a precipitate occurs. If a large precipitate results, add 3 cu. mm. more of potassium chromate solution and 15 cu. mm. of ethyl alcohol. Cool the solution, oscillate on the vibrator one minute, allow to stand one minute, and centrifuge. Estimate the amount of precipitate as in the case of barium chromate. Separate solution and precipitate, but do not wash the latter.

The necessity of the performance of a confirmatory test for barium depends upon the quantity of strontium found (5). If strontium is either absent or present in a small quantity, formation of precipitate P152 is sufficient proof of the presence of barium.

**CONFIRMATION OF BARIUM.** Dissolve barium chromate precipitate P152 in a cone with 5 to 10 cu. mm. of hydrochloric acid. Add 5 cu. mm. of 4 *M* sulfuric acid, stir, and centrifuge. Remove the solution and wash with three portions of 0.1 *M* nitric acid to remove all traces of calcium, as these interfere with the later formation of barium sulfate crystals. To the precipitate add such an amount of concentrated sulfuric acid as to form a mixture containing 5 micrograms of barium per cubic millimeter of solution. Stir the mixture, remove 5 cu. mm. of the slurry obtained with a capillary pipet, and place on a slide. Heat the slide over a microburner until dense white fumes are evolved and allow to cool. If crystals do not appear in a few minutes, breathe once or twice over the solution. If crystals are too small, repeat the heating of the test drop as described above. The characteristic forms of the crystals of barium sulfate and strontium sulfate are shown in the photomicrographs (Figures 1 to 4). Sulfuric acid which has stood in a small reagent bottle for some time should not be used for this test (4).

**CONFIRMATION OF STRONTIUM.** To strontium chromate precipitate P154 add 25 cu. mm. of 3 *M* sodium carbonate solution and heat on the steam bath with stirring for 10 minutes. If more than 50 micrograms of strontium are present, repeat the treat-



ment with another 25-cu. mm. portion of the sodium carbonate solution. Centrifuge, separate the solution and precipitate, and wash with three 5- to 10-cu. mm. portions of 3 *M* sodium carbonate solution. Add sufficient hydrochloric acid to dissolve the precipitate and evaporate in small portions on a slide. Test the residue for strontium by the method of Adams (1). [The nitrite reagent is prepared by mixing equal volumes of potassium nitrite solution and acetate buffer solution. The former contains 500 grams of potassium nitrite in 1 liter. The latter is prepared by adding 450 grams of sodium acetate trihydrate (or 325 grams of potassium acetate) and 100 ml. of glacial acetic acid to sufficient water to make 1 liter of solution. The mixed reagent decomposes slowly, but if kept in a stoppered microcone it may be used for several days.]

Moisten the residue with a solution of cupric nitrate or cupric acetate which contains a quantity of cupric ion equal to five times that of the strontium present. Evaporate the mixture to dryness. When the slide has cooled to room temperature treat the residue with a small volume of the new nitrite reagent (1). The appearance of small green squares—probably a triple nitrite of strontium, copper, and potassium—confirms the presence of strontium. The use of transmitted light of high intensity is essen-

tial for the recognition of the color of the crystals under the microscope. The green squares of the strontium compound separate a few minutes after addition of the nitrite reagent. Barium, calcium, and magnesium do not give the test. If a nitrite solution containing 1,000 grams of potassium nitrite per liter is used, the strontium test is more sensitive, but calcium interferes by forming a few green crystals. Barium does not form green crystals but interferes with the strontium test if the quantity of barium present is ten times that of strontium.

**SEPARATION OF CALCIUM FROM MAGNESIUM.** Add 50 cu. mm. of water to solution S154, stir, add 3 cu. mm. of 1.5 *M* potassium oxalate, and unless a precipitate has already occurred, let the mixture stand about 15 minutes. If a precipitate separates, heat the mixture to 70° to 80° C. and add gradually 3 to 10 cu. mm. more of potassium oxalate solution, adjusting the total volume of the reagent to the size of the carbonate precipitate. Heat for 5 minutes, centrifuge at once, and separate the solution with a capillary siphon. Wash the precipitate with two portions of water. Estimate the amount of calcium present by comparing with a known amount of calcium oxalate.

**CONFIRMATION OF CALCIUM.** Dissolve precipitate P156 with such an amount of 6 *M* hydrochloric acid as to form a solution

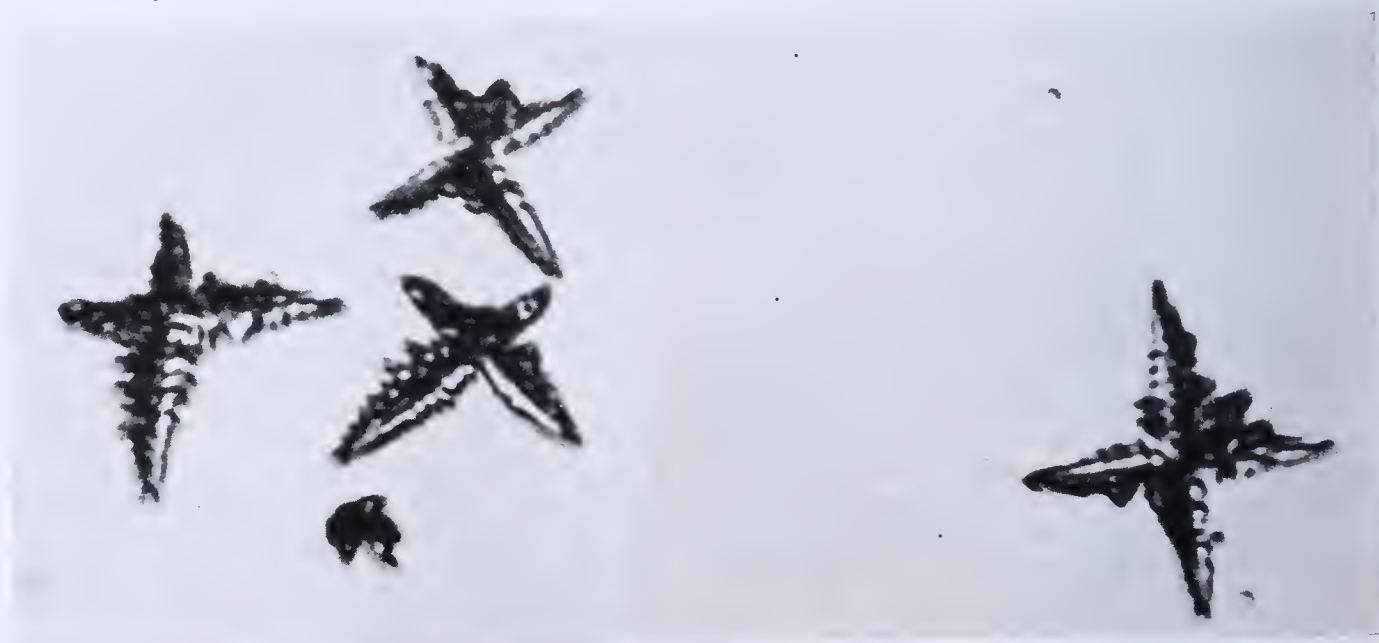


FIGURE 1. CRYSTALS OF BARIUM SULFATE  
1,180 times actual size



FIGURE 2. STRONTIUM SULFATE CRYSTALS  
800 times actual size



containing approximately 5 micrograms of calcium per cubic millimeter of solution. Place the solution on a slide and near it place 1 cu. mm. of 4 *M* sulfuric acid. By means of a glass thread draw a narrow channel of liquid connecting the two solutions. If calcium is present, a microscopic examination of the test solution will show the gradual appearance of crystals of calcium sulfate dihydrate such as those shown in the photomicrograph.

In very dilute solutions the crystals form only on complete evaporation of the test drop.

**DETECTION OF MAGNESIUM,** To solution S156 add 5 cu. mm. of 15 *M* ammonia and 25 cu. mm. of 0.3 *M* disodium phosphate. Cool, and allow to stand 0.5 hour with frequent shaking and oscillating on the vibrator. The presence of magnesium is indicated by the appearance of a white precipitate of magnesium am-

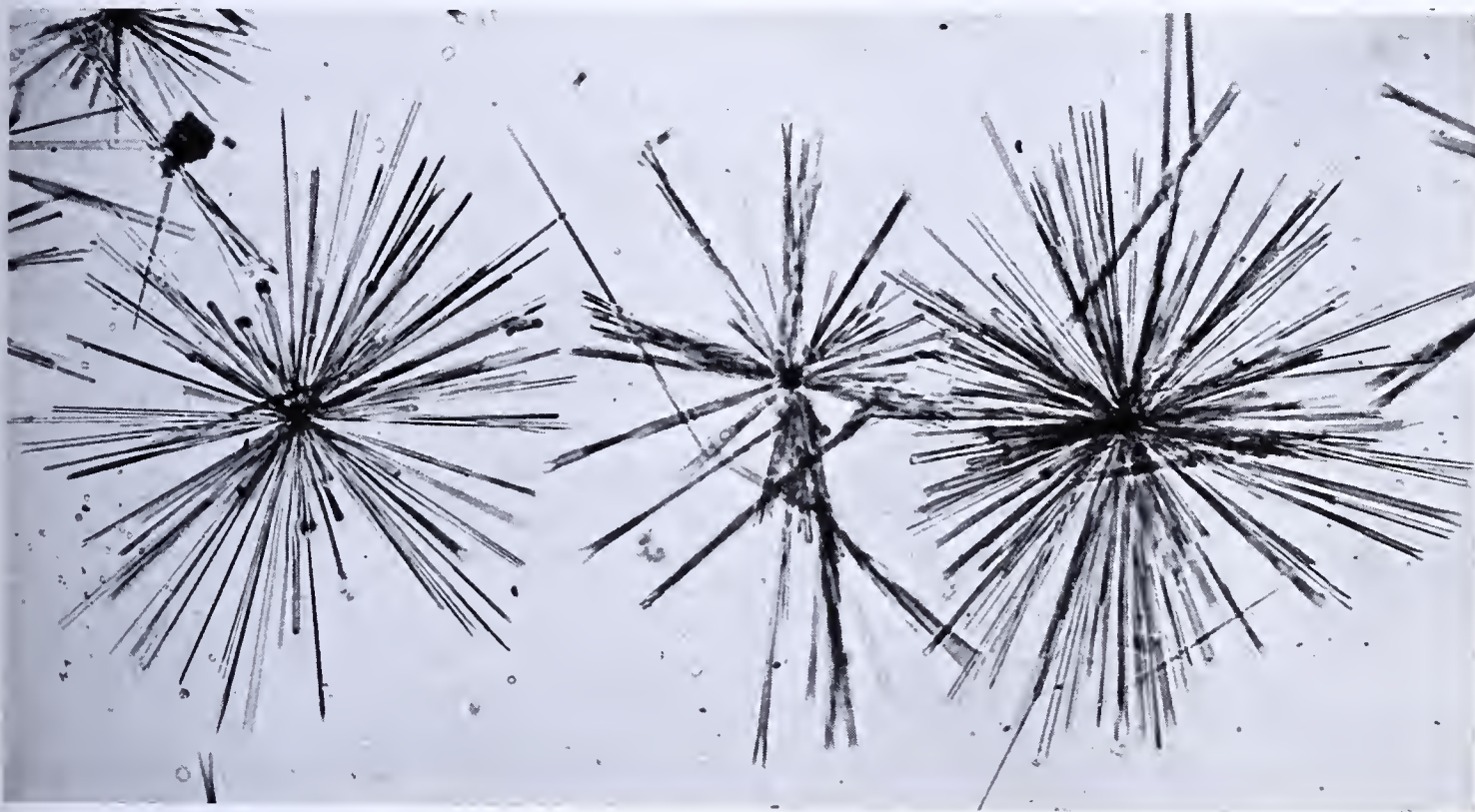


FIGURE 3. CRYSTALS OF  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$   
120 times actual size



FIGURE 4. CRYSTALS OF  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$   
250 times actual size



TABLE I. TYPICAL MICROQUALITATIVE ANALYSES OF ALKALINE EARTH GROUP

	Barium Present Found		Strontium Present Found		Calcium Present Found		Magnesium Present Found	
	Micrograms		Micrograms		Micrograms		Micrograms	
1	0	0	10	10	20	20	10	15
2	0	0	0	0	10	5	100	75
3	140	120	20	20	50	85	0	0
4	5	5	200	150	0	0	0	0
5	0	?	200	175	200	150	5	5
6	0	0	200	200	5	5	200	175
7	200	150	0	0	0	0	200	150
8	5	10	50	60	10	10	20	20

	Separation in Cone		Confirmatory Tests on Slide			
Limiting proportions	Ba:Sr = 1:1,000 (5)		Ba:Sr = 1:5 (Ba)	Ca:Ba = 1:40 (Ca)		
	Sr:Ca = 1:500 (5)		Sr:Ba = 1:10 (Sr)	Mg:Ca = 1:50 (Mg)		
	Sr:Mg = 1:500 (5)		Ca:Sr = 1:40 (Ca)	Ca:Mg = better than 1:50 (Ca)		
	Ca:Mg = 1:300 (5)					

monium phosphate hexahydrate. Centrifuge and compare the volume of precipitate with one of magnesium ammonium phosphate hexahydrate obtained from a known quantity of magnesium. Wash the precipitate once with 95 per cent ethyl alcohol.

**CONFIRMATION OF MAGNESIUM.** Dissolve precipitate P158 in such an amount of 6 M acetic acid as to form a solution containing 5 micrograms of magnesium per cubic millimeter. Place all or a portion of the solution on a slide and expose to fumes of ammonia. The presence of magnesium is confirmed by the slow crystallization of magnesium ammonium phosphate hexahy-

drate which, when seen through the microscope, has the appearance shown in the photomicrograph.

About forty solutions were analyzed in accordance with the above scheme and Table I shows eight representative results, as well as the limiting proportions of the main and confirmatory tests if made according to the scheme. In the case of the confirmatory tests, the elements in parentheses indicate those for which the tests are made. The limits of identification were: for separations, approximately 1 microgram; for confirmatory tests, barium and strontium 0.1 microgram, calcium 0.04 microgram (2), and magnesium 0.001 microgram (2).

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## Drying Etched Lead Surfaces

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**I**N DEVELOPING a routine procedure for microscopically studying the crystalline structure of lead cable sheathing, difficulty was experienced in suitably drying the etched lead samples without formation of a film of oxide. It was found that an unoxidized surface could be maintained by submerging the etched lead sample in a 2 per cent solution of glacial acetic acid, but this necessitated the use of an accessory water-immersion lens. As a result a great portion of light reflected by the metallic surface was absorbed by the water and lenses; thus longer exposures were required when photographing and greater difficulty was experienced in focusing the camera.

In order to avoid the inconvenient water-immersion method, drying the etched sample in a blast of warm air after rinsing in alcohol and ether, and drying after rinsing in acetone were tested. During the process of drying by these methods, the etched lead surface was considerably oxidized.

A simple method of drying which minimizes oxidation is here described. This is part of a routine procedure used constantly in this laboratory in examining structure of lead cable sheathing. A brief description of the method long used in the Buffalo Niagara Electric Testing Laboratory for etching lead cable sheathing is also included, in order to afford a more complete picture of the entire etching process. The procedure for preparation of lead cable sheathing for microscopic examination is intended for lead containing small amounts of impurities. It is straightforward and will yield good results if care is taken.

### Preparation of Sample for Etching

The section of lead sheathing to be studied is microtomed (2) on a Spencer Lens Company microtome No. 860, taking care that the lead is not scratched during this process. The angle of inclination of the microtome blade with the horizontal is made as small as possible while still obtaining a satisfactory cut. Sections 2 microns thick are sliced off at a time. If the microtome blade is feather-edged, it will easily be nicked and scratching of the lead will result.

### Etching of Sample

A well-known solution (1) for etching is used, containing 15 ml of glacial acetic acid, 20 ml. of concentrated nitric acid, and 80 ml of water.

The microtomed sample is placed in freshly prepared etching solution, the temperature of the latter being approximately 42° C. The sample is frequently removed from the solution, rinsed in cold water, and swabbed. Frequent visual observation of the rinsed sample will show how the etching is progressing. In the final stage, the crystals appear mirrorlike when viewed with the naked eye. When the etching process is near the desired stage the specimen is observed through the microscope to ascertain whether or not further etching is necessary. During etching the microtomed surface must not be exposed to air, but should be kept covered with a film of water when out of the etching solution. Since the thickness of the worked layer of lead resulting from microtoming is small, the etching process will consume only a short time, and any deep scratching resulting from microtoming will not disappear with the worked layer.

### Drying of Sample

If the sample is not dried properly after being etched, the surface will quickly oxidize before a photograph can be taken. The following is a sure method of drying lead etchings, which is very easily performed and takes only a minute or two:

After quickly rinsing the sample in tap and distilled water, it is placed in a 130-ml. (4-ounce) bottle and covered with U. S. F. acetone. The bottle is stoppered with rubber through which is thrust a piece of glass tubing connected by means of a piece of pressure tubing to a water suction pump. The acetone vapor is drawn out by suction for a short time, the bottle is then inverted and the acetone is drawn out. After a short time all the acetone vapor will be removed and the sample will become dry and may then be photographed in air. Lead surfaces dried in this way will remain intact for several days or more.

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# INDUSTRIAL and ENGINEERING CHEMISTRY

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## Analytical Methods for Methyl Bromide

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Methods are presented for determining methyl bromide in air and in products for which it is used as a fumigant. The Beilstein test made with a commercial methanol torch serves for rapid detection, and with artificial standards may be employed for semiquantitative estimation in the range 50 to 500 p. p. m. More accurate results are obtained by means of ethanolamine hydrolysis and bromide determi-

nation. The Kolthoff-Yutzy procedure is used for amounts in the above range, and the Volhard titration for greater concentrations. For the analysis of fumigated products, the Kolthoff-Yutzy method is applied after ashing with alcoholic potassium hydroxide in the presence of sodium chloride. Recoveries average 96 per cent on knowns with 1 mg. of bromide per 10 grams of flour, nuts, dried fruits, or tobacco.

SINCE the recent introduction of a pure grade of methyl bromide in commercial quantities, this compound has found increasing application, particularly as a fumigant (9). In the course of research on it at the Dow Laboratories, several analytical problems have arisen; as progress toward the solution of these may be of general interest, results accumulated during the past two years are summarized here. The problems studied deal with the determination of methyl bromide in fumigated products and in air, both at migrating concentrations and at greater dilution.

### Handling of Methyl Bromide

Precautions in handling methyl bromide are necessary, since the vapors are toxic if inhaled in excessive amounts. Prolonged exposure to low concentrations should also be avoided. Operations with open containers should be carried out only in a thoroughly ventilated place. For preparing small samples the procedure is as follows:

Soft-glass bulbs are blown from finely drawn tubing and bent as shown in Figure 1, A. The volume of the bulb should not exceed too greatly that of the sample desired, in order that air buoyancy corrections may be kept low. A supply cylinder of commercial methyl bromide (99.7 per cent pure by bromine assay) is kept in an efficient hood. Liquid from the cylinder is transferred to a small test tube (1 × 5 cm.) surrounded by lumps of solid carbon dioxide. The tip of a tared sample bulb is dipped into the methyl bromide and the bulb quickly cooled in an acetone-solid carbon dioxide bath. Intermittent warming and cooling serve nearly to fill the bulb if desired; or by inverting, some liquid may be blown out to obtain a smaller sample. The tip is sealed off while the bulb is again cooled, then placed under a vacuum to reach room temperature before reweighing. From a number of such samples, the desired weights can be selected for use in small fumigation test chambers.

### Detection in Air

For the protection of those working with methyl bromide, it is important to have a simple procedure capable of indicat-

ing quickly the presence of dangerous concentrations. The well-known Beilstein test for organic halide vapors is satisfactory. All that is necessary is a flame impinging on a copper strip; in the presence of methyl bromide or other halide vapor, the flame becomes green or blue. Obviously the fuel supply should be kept free from halogen.

TABLE I. DETECTION OF METHYL BROMIDE WITH LAMP

Methyl Bromide Present <sup>a</sup> P. p. m.	Flame Color	Monobromobenzene	
		20° C.	30° C.
		Ml./100 ml. mineral oil	
0	Almost invisible	0	0
50	Faint green	0.9	0.5
100	Moderate green	1.8	0.9
200	Strong green with trace of blue	3.5	1.8
500	Blue-green	8.5	4.3
1000	Strong blue	17.0	8.5

<sup>a</sup> Concentrations expressed in parts per million by volume have been calculated for 760 mm. of mercury and 25° C., assuming the ideal gas law to be valid.

A commercial methanol torch appeared most practical for general use. The one selected is a self-generating burner which had been designed for detection of halide refrigerant leaks and is equipped with a sampling tube and copper cone. (This torch, known as the Frigidaire halide leak detector, SA-2136, is available at a nominal price from the Frigidaire Division, General Motors Sales Corp., Detroit, Mich.) The sensitivity varies with different rates of combustion, maximum sensitivity being obtained with a low flame. This is somewhat too delicate for the purpose; hence the valve is adjusted arbitrarily so that with pure air the inner flame just disappears within the copper cone. Under these conditions the outer flame exhibits colors as shown in Table I, when air containing methyl bromide enters the sampling tube.

As comparison standards for indicating the appearance of the flame at various concentrations, solutions of monobromobenzene in clear heavy paraffin oil are useful. To 100-ml.



portions of the oil are added the volumes of bromobenzene shown in Table I. The solutions are kept in containers of at least 500-ml. capacity and should be shaken well before use. The vapor pressure of bromobenzene above each solution at the given temperature is such that when the sampling tube is inserted, the flame assumes the characteristics shown by the corresponding methyl bromide-air mixture.

Contamination of the sampling tube must be avoided, and opportunity allowed for copper bromide to burn out of the torch between analyses. Naturally the air drawn through standards should be free from methyl bromide. Light conditions under which samples and standards are observed should be as nearly identical as possible.

With a torch operating, the approximate concentration of methyl bromide in air can be told at a glance. A strong green flame tinged with blue is evidence of an unsafe concentration. The method has been useful in this laboratory for detecting cylinder leakage, roughly checking diffusion rates, and following the aeration of fumigated products. Other volatile organic halides also respond to this test, which is not specific for methyl bromide.

### Determination in Air

For a more exact determination of methyl bromide at fumigating concentrations (16 to 48 mg. per liter; 1 to 3 pounds per 1,000 cubic feet), methods based on hydrolysis and subsequent halogen determination offer the easiest attack. In early experiments alcoholic potassium hydroxide was employed in a refluxing apparatus, the liberated bromide being titrated argentometrically. Busbey and Drake (1) modified this method by applying an iodometric bromide determination (8), giving the advantages of greater sensitivity and specificity. Unfortunately the hydrolysis is slow and the apparatus cumbersome.

Rauscher (11) has recently described the use of mono-ethanolamine in halogen determinations. Trial of this reagent revealed that methyl bromide decomposes in it faster than in alcoholic alkalis. For practical purposes the reaction is complete after 15 minutes at room temperature, making possible a simple procedure. It is necessary only to take the sample, expose to ethanolamine, and determine bromide by the Volhard method (4) or by Kolthoff and Yutzy's modification (6) of van der Meulen's method (10). The former is more rapid, while the latter requires elimination of the ethanolamine but is more sensitive and specific, since chlorides do not interfere. In practice, the Volhard method is used for samples containing more than 5 mg. of methyl bromide, and the Kolthoff-Yutzy procedure is employed for smaller amounts.

An air-sampling device capable of allowing exposure to ethanolamine is necessary. The authors have used evacuated 2-liter flasks, through the stopcock of which 3 ml. of reagent may be introduced after sampling. A  $\frac{1}{8}$  29/42 joint between flask and stopcock provides for easy removal of the hydrolyzed sample. The commercial lubricant Lubriseal is satisfactory for the stopcock, but only ethanolamine should be placed on the glass joint, especially if the Kolthoff-Yutzy method is to be employed. For sampling without vacuum apparatus, calibrated wide-mouthed glass-stoppered bottles of about 1-liter capacity are useful. Samples are introduced by placing the bottles within the chamber to be tested and pumping with a plunger, shown in Figure 1, B and C. The plunger is made from brass tubing and a rubber sheet about 2 mm. thick, slightly smaller in diameter than the bottle. Slits in the rubber permit easy entrance through the bottle neck, while a section of a rubber stopper on the tube end prevents breakage. About 20 strokes serve to change the air completely; then a sealed soft-glass bulb containing 2 ml.

of ethanolamine is introduced, the stopper inserted, and the bulb broken by shaking. After 15 minutes or longer for hydrolysis, either halogen method may be applied.

**VOLHARD METHOD.** The stopper and sides of the apparatus are washed down with about 30 ml. of water, and a measured amount of standard silver nitrate (0.02 or 0.1 *N*, depending on the amount of bromide expected) is introduced, with enough 6 *N* nitric acid to provide a 1- to 3-ml. excess. At this point silver bromide precipitates if methyl bromide was present in the sample. The excess silver nitrate is titrated with standard 0.02 or 0.1 *N* thiocyanate, using the customary ferric alum indicator (4). A blank on the same amount of ethanolamine should be carried through the procedure and allowed for in calculating the results, since ethanolamine slightly retards the end point. Ethanolamine also sensitizes silver bromide to the action of light, which should be avoided as much as possible. Dark precipitates may be filtered off before back-titration. One milliliter of 0.100 *N* silver nitrate is equivalent to 9.50 mg. of methyl bromide.

Mg. of  $\text{CH}_3\text{Br}$  per liter  $\times 0.0625$  = pounds per 1000 cubic feet.  
Mg. of  $\text{CH}_3\text{Br}$  per liter  $\times 258$  = parts per million (calculated for 760 mm. and 25° C.)

This procedure was tested in two ways: (1) By means of heavy glass rod inserted through a rubber stopper, a methyl bromide sample bulb was crushed within a bottle, after which an ethanolamine bulb was broken by shaking; (2) a steel drum of 118-liter capacity, fitted with a bulb-breaking device and small electric fan, was sampled directly by the methods indicated. The former procedure was used to check the completeness of hydrolysis, with results as shown in Table II. The latter includes sampling errors and corresponds more closely to actual practice. In this case, usually one or more open bottles were placed inside the drum before each run and another sample was taken through a tube leading to the evacuated flask. These data are included in Table III.

**KOLTHOFF-YUTZY METHOD.** All ethanolamine must be removed prior to the bromide determination; otherwise organic bromides are formed, causing low results. Attempt

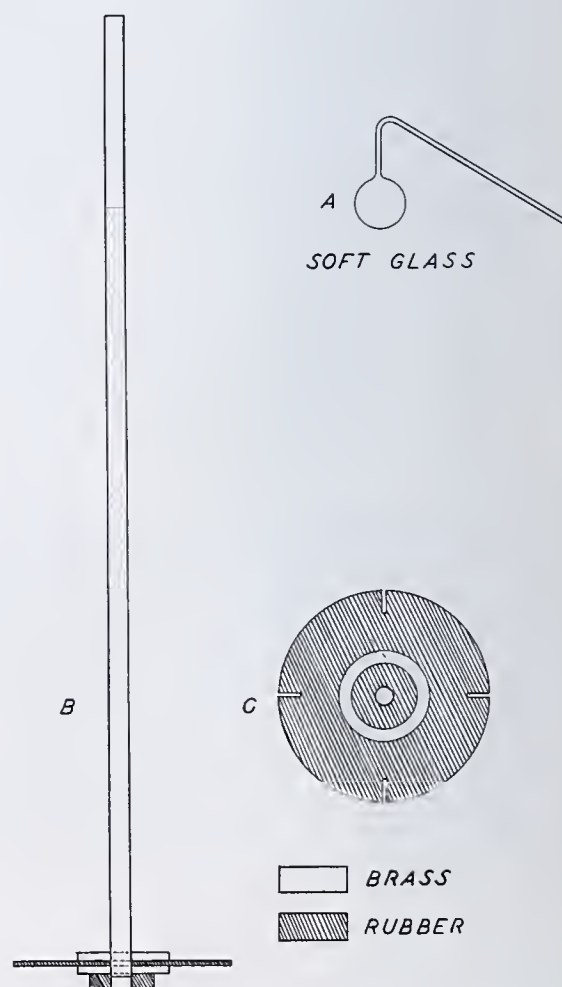


FIGURE 1. BULB AND PLUNGER



TABLE II. BOTTLE EXPERIMENTS, VOLHARD METHOD

Bottle Volume Ml.	CH <sub>3</sub> Br Taken Mg.	CH <sub>3</sub> Br Found Mg.	Error Mg.	%
515	5.6	5.6	0.0	0.0
1026	20.3	20.2	-0.1	-0.5
515	23.3	23.2	-0.1	-0.4
515	38.0	38.0	0.0	0.0
515 <sup>a</sup>	53.6	53.2	-0.4	-0.8
1030	199.0	197.8	-1.2	-0.6

<sup>a</sup> 10-minute hydrolysis; all others allowed 15 minutes.

TABLE I DRUM EXPERIMENTS, VOLHARD METHOD

CH <sub>3</sub> Br Taken Mg./l.	Sampling Method	Hydrolysis Time Min.	CH <sub>3</sub> Br Found Mg./l.	Error Mg./l.	%
10.8	1-l. bottle	30	10.7	-0.1	-0.9
10.8	2-l. flask	30	10.8	0	0
16.1	1-l. bottle	15	16.0	-0.1	-0.6
19.9	1-l. bottle	15	19.9	0	0
19.9	2-l. flask	25	19.8	-0.1	-0.5
21.3	1-l. bottle	15	21.4	+0.1	+0.5
21.3	2-l. flask	20	20.8	-0.5	-2.4
23.8	1-l. bottle	15	23.5	-0.3	-1.3

at simple evaporation failed because of oxidation of some ethanolamine to nonvolatile and brominatable compounds. This oxidation takes place more rapidly at higher temperatures and in more alkaline solutions. The procedure found most reliable consists in adding sodium bicarbonate to hold bromide, boiling off most of the water, then rapidly expelling the remaining water and ethanolamine by heating in a current of steam. The steam displaces oxygen and aids in sweeping out vapors. A well-ventilated hood is necessary to remove the dense fumes of ethanolamine. By the use of an exit tube and condenser these may be avoided, but the operation is then much slower. Mechanical losses by bumping must be guarded against; the addition of a little sodium chloride lowers the magnitude of such losses, although increasing the tendency to bump. Bumping may be reduced by heating flasks from the sides instead of the bottom, as dryness approaches.

**Reagents.** Ethanolamine. The chief requirement is that no organic residue be left after evaporation in steam as above. Fresh products from the Eastman Kodak Company have been satisfactory, but on standing yellow oxidation compounds sometimes formed and were removed by distillation in a nitrogen atmosphere.

Sodium chloride, a saturated solution of the c. p. product.

Sodium bicarbonate, c. p. powder.

Sodium acid phosphate, c. p. NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O crystals.

Hypochlorite solution, 1 N sodium or potassium hypochlorite or 0.1 N sodium or potassium hydroxide (6, 10).

Sodium formate, 50 grams of c. p. sodium formate in water to make 100 ml.

Sodium thiosulfate, 0.01 N solution stabilized with 1 gram of sodium carbonate per liter. Standardized against 0.01 N potassium iodate using 75 ml. of water, 10 ml. of 6 N sulfuric acid, and 0.5 gram of pure potassium iodide.

Sodium molybdate, 1 gram per 100 ml.

Potassium iodide, c. p. crystals.

Starch indicator, prepared according to Kolthoff (5).

Sulfuric acid, 6 N.

**Procedure.** The hydrolyzed sample is washed into a 250-ml. Erlenmeyer flask and treated with 0.5 ml. of saturated sodium chloride solution and approximately 0.5 gram of sodium bicarbonate. By evaporation over a flame or on a hot plate the volume is reduced to not less than 10 ml.; then the evaporation is quickly continued to dryness by heating while steam is blown through the flask. Constant swirling is necessary to prevent bumping, and at the end all ethanolamine must be driven from the sides of the flask. With the steam off, the flask is allowed to cool; then it is steamed again without external heating until the salt redissolves. The steam tube is rinsed with water and the volume brought to about 50 ml.

To the solution are added 2.5 ml. more of the saturated sodium chloride, about 1 gram of sodium acid phosphate, and

2 ml. of hypochlorite, and the mixture is heated to boiling. After a minute or so, 2 ml. of formate solution are introduced and boiling is continued for 2 minutes. The sample is cooled, diluted to 75 ml., and treated with one drop of molybdate solution, 0.5 gram of potassium iodide, and 10 ml. of 6 N sulfuric acid. Titration should be made immediately with standard thiosulfate, starch indicator being added just before the end point. A blank on ethanolamine with all other reagents should be carried through the entire procedure and subtracted. One milliliter of 0.010 N thiosulfate is equivalent to 0.1583 mg. of methyl bromide.

Drum tests of this procedure are listed in Table IV. The data reveal bromide losses which are small in actual amount, but relatively large in percentage. Fortunately, in this range (50 to 500 p. p. m.) absolute accuracy is rarely necessary. Experiments on evaporating ethanolamine with known amounts of potassium bromide indicate that most of the error lies in this step, and may be due both to mechanical loss and to residual traces of organic matter. Other amines which can be evaporated without decomposition were studied, but none was as efficient in its hydrolyzing action as ethanolamine. Likewise, other buffers than sodium bicarbonate were tried for binding the bromide, without success in improving the method. If more accurate results are necessary, one may obtain corrections for bromide losses by carrying out the evaporation procedure with known inorganic bromides and ethanolamine.

TABLE IV. DRUM EXPERIMENTS, KOLTHOFF-YUTZY METHOD

CH <sub>3</sub> Br Taken Mg./l.	Sampling Method	Hydrolysis Time Min.	CH <sub>3</sub> Br Found Mg./l.	Error Mg./l.	%
0.218	1-l. bottle	20	0.198	-0.020	-9.2
0.218	2-l. flask	20	0.189	-0.029	-13.3
0.381	1-l. bottle	20	0.374	-0.007	-1.9
0.381	2-l. flask	20	0.379	-0.002	-0.5
0.855	1-l. bottle	15	0.798	-0.057	-6.7
0.855	1-l. bottle	20	0.819	-0.036	-4.2
0.855	2-l. flask	20	0.821	-0.034	-4.0
1.139	1-l. bottle	15	1.104	-0.035	-3.1
1.139	1-l. bottle	20	1.111	-0.028	-2.5
1.139	2-l. flask	20	1.113	-0.026	-2.3
1.661	1-l. bottle	15	1.618	-0.043	-2.6
1.661	1-l. bottle	20	1.611	-0.050	-3.0
1.661	2-l. flask	20	1.609	-0.052	-3.1

Determination of Bromide in Fumigated Products

During fumigation with methyl bromide, most products absorb minute amounts of bromine. There is evidence that the greater part of this exists in the form of inorganic bromide, rather than as dissolved or adsorbed methyl bromide. Studies are being conducted to ascertain the state of all this bromine; meanwhile it is important to have a method for determining the total held by various products, especially by foodstuffs. Several procedures tried indicated that ashing with alcoholic potassium hydroxide is the most promising for securing all bromine free from organic matter. Details presented here were chosen with the aim of making the method applicable to materials of widely varying character.

Since nearly all natural products contain considerable chloride, the method chosen must be capable of determining bromide in its presence. The Kolthoff-Yutzy procedure (6) fulfills this condition and provides the sensitivity required for the small amounts involved. The fact that iodine behaves in the same manner as bromine is of no consequence, since only traces are likely to be present and the principal object is to measure increases in bromide content resulting from fumigation. This purpose is served by the use of unfumigated controls which are analyzed along with the fumigated samples, the difference being due to bromine gained through exposure to methyl bromide.

REAGENTS required are the same as those listed above, omitting ethanolamine and sodium bicarbonate, and adding alcoholic



TABLE V. DETERMINATION OF BROMINE IN VARIOUS PRODUCTS

Sample	Br Added Mg.	Br Found Mg.	Br Found Corrected for Blank Mg.	Error Mg.	%
Dried raisins	0	0.068	...	...	...
	0.974	1.018	0.950	-0.024	-2.5
	0.974	0.999	0.931	-0.043	-4.4
	0.974	0.989	0.921	-0.053	-5.4
Whole-wheat flour	0	0.090	...	...	...
	0.974	1.040	0.950	-0.024	-2.5
	0.974	1.074	0.984	+0.010	+1.0
	0.974	1.054	0.964	-0.010	-1.0
Pecan nut meats (unsalted)	0	0.045	...	...	...
	0.974	0.983	0.938	-0.036	-3.7
	0.974	0.983	0.938	-0.036	-3.7
	1.948	2.000	1.955	+0.007	+0.4
Dried peaches	0	0.107	...	...	...
	0.974	1.106	0.999	+0.025	+2.6
	0.974	1.038	0.931	-0.043	-4.4
	0.974	1.033	0.926	-0.048	-4.9
American cheese	0	0.053	...	...	...
	0.974	0.999	0.946	-0.028	-2.9
	0.974	0.980	0.927	-0.047	-4.8
	0.974	0.992	0.939	-0.035	-3.6
Tobacco <sup>a</sup> (cured light burley)	0	0.196	...	...	...
	0.974	1.128	0.932	-0.042	-4.3
	0.974	1.118	0.922	-0.052	-5.3
	0.974	1.144	0.948	-0.026	-2.7

<sup>a</sup> For tobacco the samples were 5 grams; for all others, 10 grams.

potassium hydroxide, 2 grams per 100 ml. of 95 per cent ethyl alcohol; potassium fluoride, c. p.  $\text{KF} \cdot 2\text{H}_2\text{O}$  crystals; hydrochloric acid, about 0.2 *N* (1 to 50); and sodium hydroxide, 2 grams per 100 ml.

For containing the samples during ashing, silica dishes are to be preferred. Those used in this laboratory are 8 cm. in diameter and 2.5 cm. deep, with flat bottoms. Glassware may be used but has much shorter life; platinum dishes are satisfactory. The muffle used for ashing should be provided with temperature controls. Provision for introducing a slow stream of oxygen during ignition is also desirable, as it reduces the time required for complete combustion.

**PROCEDURE.** An appropriate sample (5 to 10 grams), ground if necessary to ensure uniformity, is weighed out in a silica dish and treated with 3 ml. of saturated sodium chloride and 40 ml. of alcoholic potassium hydroxide, evenly distributed. After evaporation of the alcohol, preferably on a steam bath, the sample is dried for a short time at 110° C., then ashed in a muffle at 400° C. The large amount of smoke evolved may be diminished by igniting occasionally with small pieces of burning filter paper. Care should be taken that the temperature at no time exceeds 500° C., and a bright local glowing of carbon should be avoided, although dull glowing is desirable. When no more flames appear, the muffle is brought to 500° C. and the dish allowed to remain at this temperature for 10 minutes.

Upon cooling, the residue is extracted with two 25-ml. portions of dilute hydrochloric acid (1 to 50), except in the case of tobacco samples, for which only water should be used. The extracts are filtered through coarse paper, residue and paper being washed with three 10-ml. portions of water and the filtrates caught in a 250-ml. wide-mouthed Erlenmeyer flask. The filter paper is returned to the dish and again treated with 3 ml. of salt solution and 10 ml. of alcoholic potassium hydroxide. Drying and ignition are repeated as before, and the residue is extracted with 25 ml. of dilute hydrochloric acid and three 10-ml. portions of water, catching the filtrate in the same flask as before. In the case of tobacco, water is substituted for acid in this extraction also.

The combined filtrates are neutralized with sodium hydroxide solution, adjusting to the color change of methyl orange, and are evaporated to about 75 ml. The Kolthoff-Yutzy method is followed as outlined above, beginning with the addition of phosphate. No further introduction of sodium chloride is necessary. Prior to acidification about 0.5 gram of potassium fluoride is added to combine with any iron present. One milliliter of 0.010 *N* thiosulfate is equivalent to 0.1332 mg. of bromide ion. A blank on the reagents should be subtracted if absolute values are desired, but this is not necessary if only the gain due to fumigation is to be determined.

The ashing procedure recommended is the result of numerous experiments designed to obtain the most consistent recoveries. The method outlined is capable of recovering 94 per cent or more of added bromides, in amounts of a few milligrams. Addition of salt helps to prevent mechanical and volatilization losses of bromide, and also seems to favor

complete extraction of the ash. Prior to its use, recoveries were much lower, especially in the case of tobacco, from which sometimes 30 per cent might be lost. In case hydrochloric acid is used in extracting tobacco ash, results are erratic, probably owing to interference of inorganic materials in the Kolthoff-Yutzy method. End points, normally good, exhibit pronounced return of iodine color under these conditions. Probably the same would hold true with any high-ash high-nitrogen product.

For a more rapid approximate procedure, the second ashing may be omitted and only the first filtrate analyzed for bromide. The second filtrate contains roughly 10 per cent of the total, but this figure may vary considerably. It is best to make the second ignition and extraction even though more time is required. In several tests in which a third ashing was made, the bromine found was negligible, indicating that losses other than incomplete extraction account for errors in the procedure.

Table V shows the recovery of known amounts of potassium bromide added to 10-gram samples of several products (5-gram samples in the case of tobacco). A reagent blank of 0.014 mg. of bromine has been deducted. The data in Table VI were obtained during typical fumigation experiments. They have no significance as tests of the procedure since all were run as unknowns, but are of interest in showing the magnitude of bromine absorption. The amount of bromide gained during fumigation varies considerably with methyl bromide concentration and time of exposure. Also it has been noted that unfumigated samples from different sources show variations in their bromine content. Apparently determinations of bromide have not previously been made on several of the products reported here. Leipert (7) gave a comprehensive literature review without mentioning analyses of any of them. Geddes and Lehberg (3) recently published a method applicable to water-soluble bromine in brominated flours. They reported recoveries of 93 to 97 per cent but did not mention the bromine content of untreated samples. While the results for untreated products listed in Table VI may be slightly high, owing to traces of iodine they probably indicate approximately the percentages of bromine to be expected in average unfumigated material.

TABLE VI. DETERMINATION OF BROMINE IN FUMIGATED PRODUCTS

Sample	Unfumigated Controls %	Fumigated Samples %	Gain Due to Fumigation %
Dried raisins	0.0007	0.0010	0.0003
Whole-wheat flour	0.0009	0.0100	0.0091
Pecan nut meats	0.0004	0.0199	0.0195
Dried peaches	0.0011	0.0030	0.0019
American cheese	0.0005	0.0080	0.0075
Cured tobacco	0.0039	0.0104	0.0065

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# Photocolorimetric Determination of Starch in Paper

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THE color reaction with iodine has been extensively used for the determination of starch, but careful photometric study of the reaction has been limited to one or a few varieties (1, 4, 5, 6). In a study of the determination of starch in paper, it became necessary to determine the effect on the light absorption of type and treatment of starch with special reference to starches commercially available for sizing purposes and the effects of certain extraneous materials which might be encountered in paper analysis.

The spectral absorption curves of the starch-iodine system were determined with the General Electric Hardy recording spectrophotometer (3).

The photoelectric absorption meter used employs the Weston photonic cell, which is connected through a potentiometer to a microammeter with 100 scale divisions. The light source is a concentrated filament incandescent lamp, operated at constant voltage and the light is suitably collimated before passing into the absorption cell. The photonic cell is fitted with a Jena BG18 glass filter to eliminate any effect due to infrared light, and provision is made for inserting filters of the desired spectral range. The absorption cells used in this work provide a liquid thickness of 5 mm.

## Materials

The determination of starch in paper may involve any of the raw or modified starches used for sizing purposes. Consequently, a wide variety was chosen in order to include typical specimens of all the kinds which might be encountered in practical analysis, together with certain specimens of theoretical interest. Specially prepared alpha- and beta-amylase from cornstarch (9) were also included. The canna starch was prepared from canna bulbs. The sweet potato starch was made available through the courtesy of O. A. Sjostrom. The remaining starches were selected from those commercially available. Table I shows the types of starch investigated.

TABLE I. TYPES OF STARCH INVESTIGATED	
Raw Starches	Starch Derivatives and Modifications
Arrowroot	Corn alpha-amylase
Canna	Corn beta-amylase
Corn	Corn A (chlorinated)
Potato	Corn B (chlorinated)
Rice	Corn C (dry starch treated with acid and roasted)
Wheat	Corn D (moist starch treated with acid and dried)
	Potato A (soluble, Merck, according to Lintner)
	Potato B (hot roll gelatinization)
	Potato C (hot roll gelatinization)
	Tapioca A (hot roll gelatinization)
	Tapioca B (dextrin, dry starch treated with acid and roasted)

## Procedure

The equivalent of 5 grams of oven-dry starch was accurately weighed and cold-pasted with 20 ml. of distilled water. The suspension was then added to 600 ml. of distilled water at 50° C., the whole heated to 95° C., cooled, and diluted to 1 liter. For photometric examination, the starch suspensions were prepared by adding starch, water, and iodine solutions (in the order named) from Mohr pipets into 15 × 150 mm. test tubes to a total volume of 20 ml. The contents of the tubes were mixed by inverting twice and then by careful shaking just before use.

## Analytical Results

SPECTRAL ABSORPTION CURVES OF STARCH-IODIDE. Spectral absorption curves have been published for specific starches

(1, 4). Since the available data were inadequate for the present study, additional curves for a variety of raw and modified starches were determined.

Preliminary experiments showed that, with an iodine concentration of 0.1 gram per liter and a potassium iodide-iodine ratio of 1.5 to 1 by weight, the starch concentration does not affect the position of the minimum in the absorption curve. The latter is also unaffected by small changes in potassium iodide concentration and by the presence of aluminum sulfate, although both affect the color produced (1, 4) and the total absorption. Increase of iodine content slightly shifts the position of the minimum toward the region of shorter wave length, although the shift is negligible in the application of photometric analysis.

From the results of preliminary tests and the data available in the literature, the following were chosen as the optimum conditions for examination of the spectral transmissions of the various raw and modified starches:

Starch concentration, approximately 0.1 gram per liter  
Iodine concentration, 0.1 gram per liter  
Potassium iodide-iodine ratio, 1.5 to 1

The maximum absorption for all the raw starches examined occurs over the range 560 to 640 $\mu$ m (Figure 1). Although all the curves possess the same general shape, very real and considerable differences exist in the wave lengths of maximum absorption and in the transmissions at any given point in the spectral range. If starch is modified by oxidation or by hydrolysis, the color reaction with iodine is changed but the transmission in the band of maximum absorption may not be uniformly affected. The maximum absorption, except for beta-amylase and tapioca dextrin, occurs in the range 570 to 610 $\mu$ m (Figure 2). Extreme modification (to dextrins)

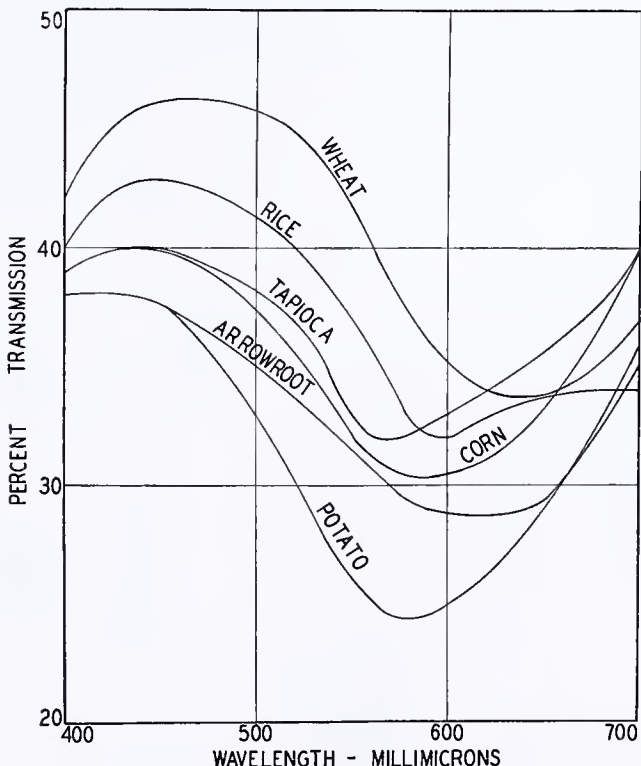


FIGURE 1. SPECTRAL TRANSMISSION OF RAW STARCHES



eliminates the region of maximum absorption and the transmission rises uniformly and rapidly in the red.

**PHOTOMETRIC ABSORPTION STUDY OF STARCH-IODINE.** On the basis of the spectral transmission data, the materials were examined further with the photoelectric absorption meter. In order to obtain a filter combination furnishing a transmission peak in the range of maximum absorption of starch-iodine, Wratten red filters Nos. 23, 25, 26, and 29 in combination with the Jena BG18 glass filter built into the instrument were examined. These provide transmission peaks of 595 to 625 $\mu$ , and all are applicable since their values approximate the maximum absorption band of starch-iodine. Filter 29, with a peak transmission of 620 $\mu$  and a range of 590 to 650 $\mu$ , was used in further work.

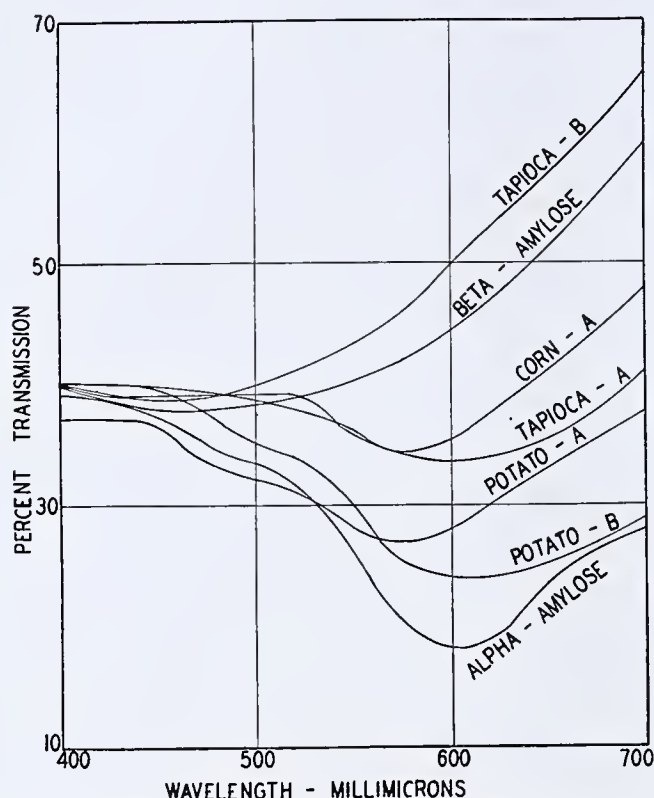


FIGURE 2. SPECTRAL TRANSMISSION OF MODIFIED STARCHES

TABLE II. MEAN SLOPE CONSTANTS AND AVERAGE DEVIATION FROM THE MEAN

Starch Type	Mean Slope Constant	Average Deviation from Mean
Arrowroot	-5.59	0.07
Canna	-4.62	0.04
Corn	-4.56	0.15
Potato	-4.91	0.05
Rice	-4.40	0.04
Rye	-4.62	0.05
Sago	-5.57	0.09
Sweet potato	-4.98	0.07
Tapioca	-4.50	0.08
Wheat	-4.84	0.03
Corn A	-3.61	0.09
Corn B	-3.92	0.06
Corn C	-3.39	0.07
Corn D	-3.68	0.07
Potato A	-4.72	0.13
Potato B	-5.92	0.06
Potato C	-6.03	0.10
Tapioca A	-4.50	0.04
Tapioca B	-1.85	0.07

Since the starch-iodine complex may be regarded as a type of chemical compound, deviations from Beer's law may be expected for some concentrations of iodine. At higher concentrations of iodine, and when suitable filters are used Beer's law is apparently obeyed—that is, the logarithm of the fractional transmission becomes proportional to the starch concentration (4, 5, 6).

Using the conditions established, transmission curves were determined for all the raw and modified starches available (Figures 3 and 4). In each case the transmission of the iodine solution with no starch present is assumed to be 100 per cent that is, the microammeter is adjusted to full scale deflection. Approximately straight-line transmission curves were obtained over the range 5 to 90 per cent transmission. Each starch has its own transmission curve of a slope which is characteristic of the starch type.

For more accurate evaluation of the transmission curves the values of  $\log T/C$  (where  $T$  is the fractional transmission and  $C$  the starch concentration in grams per liter) were calculated for each value of starch concentration used. The values of  $\log T/C$  are not absolutely constant and the deviations are characteristically different for the different starches. This is further evidence that accurate colorimetric determination of starch must be based upon a calibration curve prepared

from the same type of starch. Over the range of 5 to 90 per cent transmission the values of  $\log T/C$  do not deviate far from the mean values, and the latter, together with the average deviation from the mean, are given in Table II.

The intensity of color produced by the starch-iodine reaction is dependent upon the particle size of the starch (5). Starches characterized by large particle size show a lower transmission than those of smaller particle size. The relation under the conditions of test employed is shown in Figure 5, for which the particle size data were taken from the literature (2, 7, 8). The relation is inapplicable to modified starches.

#### Effects of Extraneous Material

Alkalies and compounds reducing iodine must be absent. Acidity due to sulfuric and hydrochloric acids is without effect over the range 1.5 to 7 pH. Opacity due to nonreactive substance

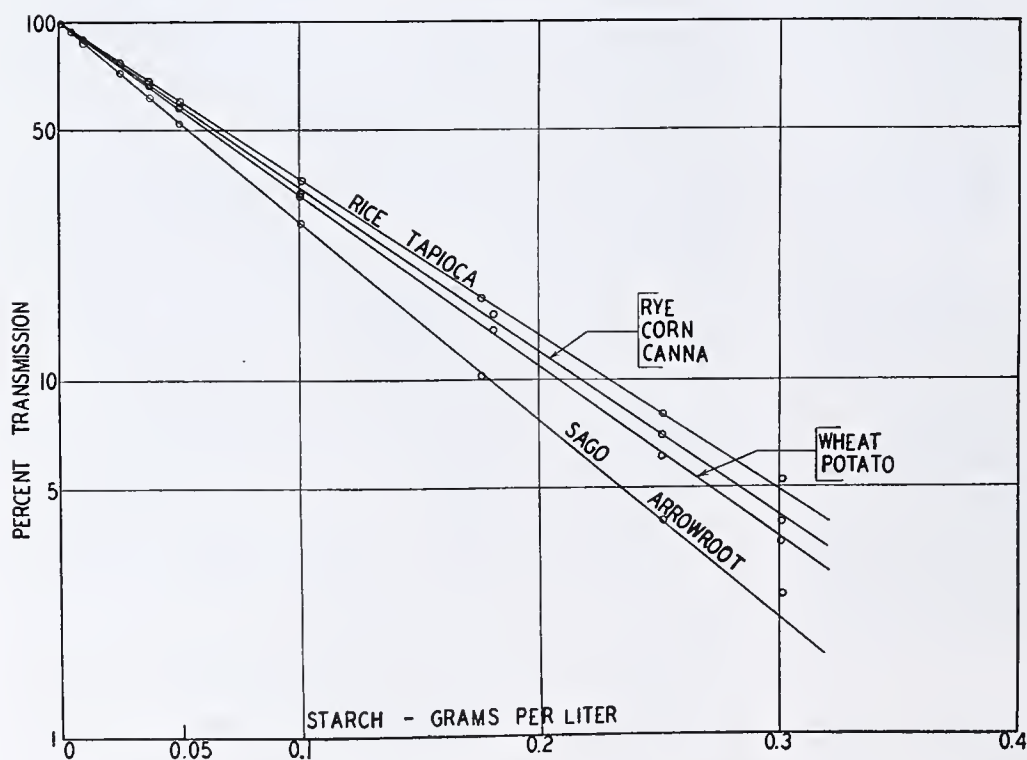


FIGURE 3. TRANSMISSION OF RAW STARCHES



such as clay may be corrected for. This may be accomplished by preparing a clay suspension of the same opacity as the paper extract as determined with the photoelectric absorption meter. The iodine solution is then added to the clay suspension and the mixture used for setting the microammeter to full scale deflection. Iodine solution is then added to the starch-containing sample and transmission measurement is made in the usual way.

For a starch concentration of 0.1 gram per liter, sodium chloride, sodium sulfate, calcium chloride, and calcium sulfate have an appreciable effect on starch-iodide transmission if the concentration is greater than 0.1 gram per liter. Aluminum sulfate, ferric sulfate, and calcium thiocyanate have an initially very large effect and quantities of 0.05 gram per liter seriously affect the system.

Gum arabic has no measurable effect; glue has little effect up to ten times the starch concentration. Lecithin and dupinol (a sulfonated alcohol) seriously interfere and the sodium stearate concentration must not exceed one-half that of the starch (Table III). The addition of any extraneous materials to starch before the addition of iodine always has a greater effect in increasing transmission than the addition of the same material after the starch-iodide has been formed. The data given in Table III were obtained upon addition of iodine to the extraneous material-starch mixture.

TABLE III. EFFECT OF EXTRANEOUS MATERIALS ON TRANSMISSION

(Cornstarch, 0.1 gram per liter)

Extraneous Material	Increase in Per Cent Transmission						
	0.05 g./l.	0.10 g./l.	0.25 g./l.	0.50 g./l.	1.0 g./l.	2.5 g./l.	5 g./l.
Sodium chloride, NaCl	0	0.1	0.5 <sup>a</sup>	0.2	0.3	2.8	10.5
Sodium sulfate, Na <sub>2</sub> SO <sub>4</sub>	..	..	..	0.3	1.0	2.0	4.5
Calcium chloride, CaCl <sub>2</sub>	..	..	..	2.5	6.4	9.2	10.7
Calcium sulfate, CaSO <sub>4</sub>	0.3	0.6	..	1.8	3.6	..	..
Aluminum sulfate, Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18H <sub>2</sub> O	1.9	3.6	5.4	4.4	4.4	4.4	4.4
Ferric sulfate, Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2.2	7.0	8.5	4.3	2.5	2.5	2.5
Calcium thiocyanate, Ca(CNS) <sub>2</sub>	2.5	4.5	10.9	16.6	21.7	31.7	37.7
Gum arabic	0.2 <sup>a</sup>	0.4 <sup>a</sup>	0.2 <sup>a</sup>	0.3	0.2 <sup>a</sup>	0.4 <sup>a</sup>	0.3
Glue	..	0.1	..	1.0	1.3	..	32.1
Lecithin	12.2	14.2	16.7	19.2	23.7	27.7	..
Dupinol	10.2	11.7	14.7	16.2	18.2	..	..
Sodium stearate	0.2	3.7	5.7	12.2	23.6	..	..

<sup>a</sup> Decrease in transmission.

## Accuracy

Provided the kind of starch and its previous treatment are known, the photocolorimetric procedure is capable of high accuracy. The nature of the starch itself is the limiting factor, and if raw starches are used, the deviation from the mean of the highest and lowest transmission curves of the starches examined may amount to  $\pm 12$  per cent. The data relating transmission to particle size (Figure 5) suggest that the latter factor is very important in determining differences in transmission of the various starches. Similarly, for modified starches (not including tapioca B dextrin), the possible error due to starch type may amount to  $\pm 25$  per cent. The influence of starch type on colorimetric methods seems not to have been generally given the consideration deserved, although Paloheimo and his associates (5) have indicated for a number of starches the error which may be introduced by

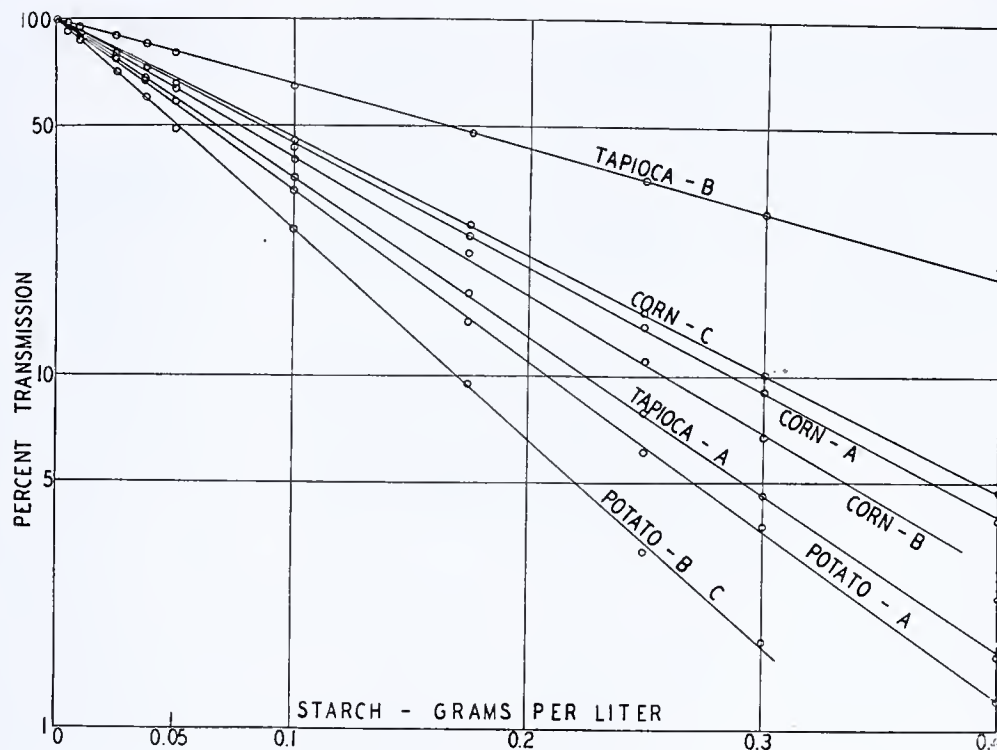


FIGURE 4. TRANSMISSION OF MODIFIED STARCHES

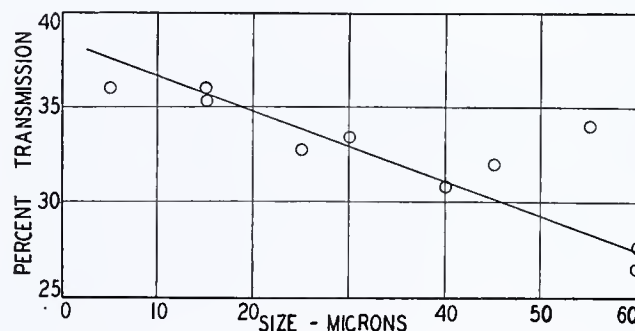


FIGURE 5. EFFECT OF PARTICLE SIZE OF RAW STARCHES ON TRANSMISSION

neglect of this factor. In the presence of dextrans, which may be present in paper together with raw or modified starches, the colorimetric method becomes totally unreliable.

In addition to alkalis and reducing materials, which must be completely absent, many other extraneous materials commonly present in paper must be in limited amount if reasonable accuracy is to be obtained in the starch determination. Methods which might be employed for the separation of starch from larger quantities of such extraneous materials (6) have not been generally applied to paper.

TABLE IV. ERROR IN STARCH DETERMINATION DUE TO EXTRANEOUS MATERIALS

Extraneous Material	Maximum Permissible Concentration for Errors Indicated		Maximum Permissible in Paper for Errors Indicated	
	For 5% error	For 10% error	For 5% error	For 10% error
	Grams/liter	Grams/liter	%	%
Sodium chloride	1.0	2.5	20	50
Sodium sulfate	1.0	2.5	20	50
Calcium chloride	..	0.5	..	10
Calcium sulfate	0.5	1.0	10	20
Aluminum sulfate	0.05	0.10	1	2
Ferric sulfate	..	0.05	..	1
Calcium thiocyanate	..	0.05	..	1
Gum arabic	5	5	100	100
Glue	1.0	1.0	20	20
Lecithin	0.05 causes more than 10% error	0.05 causes more than 10% error	1% causes more than 10% error	1% causes more than 10% error
Dupinol	0.05 causes more than 10% error	0.05 causes more than 10% error	1% causes more than 10% error	1% causes more than 10% error
Sodium stearate	0.05	0.10	1	2



Table IV gives the concentration of extraneous materials in the extract which may cause errors of 5 and of 10 per cent in the measured starch concentration, assuming a cornstarch concentration of 0.1 gram per liter. The data are derived from Tables II and III. Columns 2 and 3 are calculated on the assumption that cornstarch at a concentration of 0.1 gram per liter is analyzed. Columns 4 and 5 are calculated on the assumption that a 5-gram sample of paper is used, that the cornstarch content is 2 per cent, and that the extract is diluted to 1 liter.

Extraneous materials which must be present in quantities less than 1 to 2 per cent of the paper (Table IV) may cause serious error in the starch determination. Normally these materials are present to an extent of less than 1 per cent, but unless this is known to be true, the accuracy of the starch determination within the indicated limits cannot be assumed. Considerable error may be expected if the paper

contains acid-soluble fillers and the starch is removed by acid extraction.

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## Carotenoids in Yellow Corn

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IT IS WELL known that the vitamin A activity of yellow corn is due to the presence of carotene and cryptoxanthin, and not to the presence of the free alcohol or ester forms of vitamin A. As early as 1919, Steenbock (6) demonstrated that yellow corn was a better source of provitamin A than white corn. The experiments of Coward (3) in 1923 showed that large quantities of yellow corn are required to produce growth in rats which have been depleted of the fat-soluble vitamin A. Karrer and co-workers (4) isolated zeaxanthin, a xanthophyll, which was found to be devoid of vitamin A activity when fed to rats. Kuhn and Grundmann (5) associated the vitamin A potency of yellow corn chiefly with cryptoxanthin.

The present investigation was undertaken primarily to develop a suitable quantitative method for determining the provitamin A content of commercial samples of yellow corn. Various biological as well as colorimetric and spectrophotometric methods have been described by numerous investigators; however, none has proved entirely satisfactory as a simple, rapid, and accurate method giving reproducible results.

One of the latest proposed methods is that of Clark and Gring (2), who published data on the spectrophotometric estimation of carotenoids in yellow corn. Their samples were prepared for carotene-cryptoxanthin analysis by extraction of the pigments from the ground corn with methanol, followed by saponification. The carotene and cryptoxanthin were then separated from the xanthophylls by distribution between low-boiling petroleum ether and 90 per cent methanol. The concentration of carotene and cryptoxanthin in the epiphase was determined by means of optical density measurements at 4500 Å.

### Spectrophotometric Apparatus

The modified Bausch and Lomb visual spectrophotometer used by Buxton and Dombrow (1) was employed for determining the carotene-cryptoxanthin content of the unsaponifiable fraction of yellow corn samples. The concentration of carotene and cryptoxanthin was determined from the intensities of the absorption band at 4500 Å. by taking the mean of several readings. The extinction coefficient,  $E_1^{1\%}$ , at 4500 Å. for pure  $\beta$ -carotene in heptane is 2380 (1). A

typical absorption curve (Figure 1) for the nonsaponifiable portion of yellow corn, determined in heptane on a sample of Reid's Yellow Dent, was photographed with a Bausch & Lomb medium-sized quartz spectrophotometer equipped with a Hilger rotating sector disk and a quartz biprism. The light source was a hydrogen-discharge tube. The wave length 4500 Å. was found most desirable for determining the extinction coefficients on the carotene and cryptoxanthin fractions. Since the extinction coefficients for  $\beta$ -carotene and/or cryptoxanthin at 4500 Å. in heptane are essentially the same (Figure 1), it is possible to use the following formula for calculating the carotene and/or cryptoxanthin for a 1 per cent solution:

$$(S \times F/R \times C) = \text{gamma of carotene and/or cryptoxanthin for a 1 per cent solution}$$

where

$S$  = the screen factor

$F$  = the extinction coefficient for pure  $\beta$ -carotene or cryptoxanthin in heptane

$R$  = the reading expressed in centimeters

$C$  = the concentration

### Experimental Procedure

Weigh accurately into a digestion flask 20 grams of finely ground yellow corn and add 200 ml. of 5 per cent methanolic potassium hydroxide. Reflux on a hot plate or steam bath for at least one hour. Agitate occasionally to facilitate thorough digestion. Cool, allow the sediment to settle, and decant the supernatant liquid into a separatory funnel containing 50 ml. of water. Extract the residual sediment until the washings are colorless (usually five or six extractions are sufficient) with 50-ml. portions of purified technical heptane (1). Combine the heptane and alcoholic fractions and shake thoroughly. Remove the alcoholic layer and re-extract with 50 ml. of heptane. Combine the heptane extracts and wash free from xanthophylls and alkali by shaking thoroughly with 100-ml. portions of 90 per cent methanol; re-extract the first 90 per cent methanol wash with 50 ml. of heptane. To ensure thorough washing, examine the last methanol wash for free alkali by testing a few milliliters with phenolphthalein.

Distill the heptane portion to a small volume under reduced pressure in the presence of nitrogen gas. Add a few milliliters of isopropanol to the heptane solution before distillation to facilitate the removal of water. Make up the concentrated carotene cryptoxanthin solution to volume (50 ml.) with heptane and determine the intensity of absorption at 4500 Å. with the visual spectrophotometer.



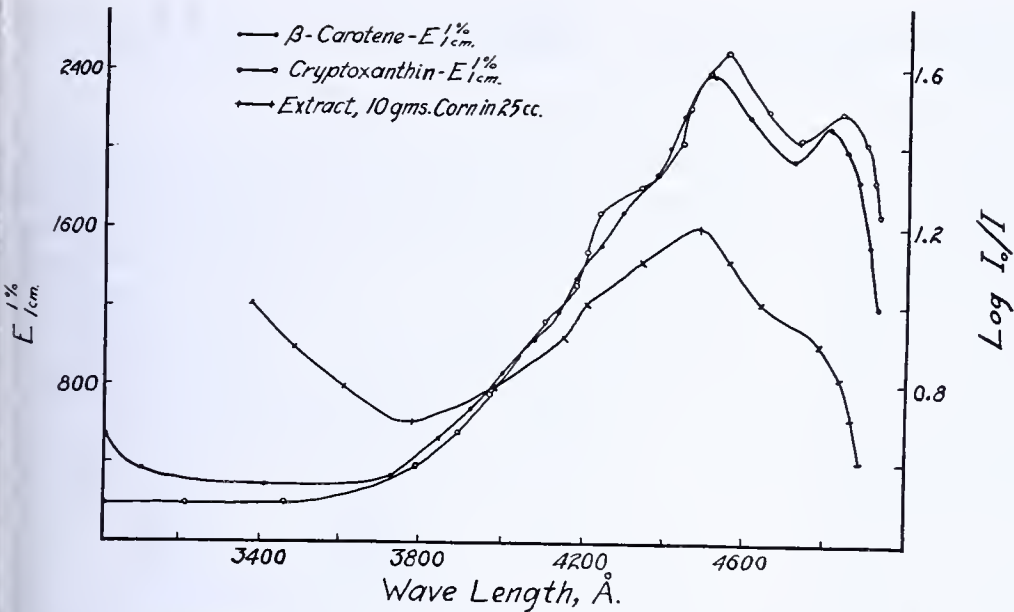


FIGURE 1. ABSORPTION SPECTRA OF CRYPTOXANTHIN,  $\beta$ -CAROTENE, AND UNSAPONIFIABLE FRACTION OF YELLOW CORN  
The solvent is heptane. The values of  $E_{1\%}^{1\text{cm}}$  for the  $\beta$ -carotene and cryptoxanthin are shown on the left ordinate; those for the  $\log I_0/I$  of the corn unsaponifiable on the right ordinate.

Chromatographic Separation of Carotene and Cryptoxanthin

No attempt has been made in this investigation to purify the 90 per cent methanol-soluble fraction (xanthophylls). Twenty-five milliliters of the concentrated carotene-cryptoxanthin solution were, however, chromatographed on a modified Tswett column and the zones developed by washing with purified heptane. Calcium carbonate (c. p. powdered), prepared by heating for 10 hours at 200° to 300° C. in the absence of oxygen and then cooling in an atmosphere of nitrogen gas, was used as the adsorbent. The apparatus used for these experiments will be described in detail in another paper. Experiments conducted on pure  $\beta$ -carotene obtained from the S. M. A. Corporation, Cleveland, Ohio, and repurified in this laboratory (m. p. 184° C. corrected, and optically inactive) and on purified cryptoxanthin (m. p. 168.6–169° C., and optically inactive) obtained chromatographically from yellow corn indicate that the carotene passes quantitatively through the adsorption column and into the filtrate, whereas the cryptoxanthin is adsorbed quantitatively by the activated calcium carbonate. The carotene fraction was reabsorbed on a column of calcium hydroxide and proved to be homogeneous.

TABLE I. CAROTENOIDS IN YELLOW CORN				
Sample	Carotene Plus Cryptoxanthin Gamma/g.	Carotene Gamma/g.	Carotene %	Cryptoxanthin %
Midwest Yellow Dent (Indiana)	5.9	0.85	14.4	85.6
Argentine yellow corn	9.3	0.70	7.5	92.5
Midwest Yellow Dent (Ohio)	4.8	0.56	11.6	88.4
Yellow corn (New Jersey)	6.9	0.48	6.9	93.1
Yellow corn (Indiana)	4.2	0.34	8.0	92.0

From the absorption curves in Figure 1, photographed with a Bausch and Lomb medium-sized quartz spectrophotometer, it is apparent that it is not possible to distinguish spectrophotometrically between carotene and cryptoxanthin when they occur simultaneously. The extinction coefficient,  $E_{1\%}^{1\text{cm}}$ , at 4520 Å. for purified cryptoxanthin in heptane, as calculated from the absorption curve in Figure 1, is 2430. By determining the intensities of absorption at 4500 Å. before and after separating the cryptoxanthin from the carotene

fraction, it was possible to calculate by difference the concentration of cryptoxanthin present. No attempt was made in this investigation to elute the cryptoxanthin from the adsorbent other than to prove that it was homogeneous and free from carotene. All the samples used for these investigations were obtained from the Nopco Experiment Station, Flemington, N. J. Duplicate examinations were carried out on each sample and, in view of the close checks obtained, the results have been averaged in Table I. Preliminary experiments carried out on each of the corn samples, using the extraction method of Clark and Gring, gave results ranging from 2 to 8 per cent lower than those reported in Table I. This discrepancy between methods may be explained by the fact that the esterified form of cryptoxanthin is less soluble in methanol than the free alcohol form and therefore complete extraction of this carotenoid would be more difficult in the method described by Clark and Gring.

Since cryptoxanthin is less efficient than  $\beta$ -carotene as a source of vitamin A, the total quantity of active carotenoids in yellow corn does not necessarily designate the actual vitamin A activity of the corn, if figured on a  $\beta$ -carotene basis. A comparison of the average results reported in Table I indicates that the provitamin A content of different samples of commercial yellow corn varies rather widely. This variation is influenced by the surface area of the kernels, which probably accounts for the greater quantity of provitamin A in the sample of Argentine yellow corn. The kernel size in this sample was considerably smaller, thus increasing the total surface or endosperm area in relation to the weight, leading to a relatively higher content of provitamin A per gram.

Summary

A simple rapid spectrophotometric method is described for determining the carotene-cryptoxanthin content of yellow corn. A chromatographic method is outlined, whereby the carotene can be separated quantitatively from cryptoxanthin. The results obtained on five commercial samples of yellow corn indicate that the carotene-cryptoxanthin contents vary considerably. A typical absorption curve for the cryptoxanthin-carotene fraction of yellow corn is reported, with a maximum at 4500 Å. Absorption curves for pure  $\beta$ -carotene and purified cryptoxanthin in heptane are given. A new extinction coefficient for pure cryptoxanthin in heptane is reported.

Acknowledgment

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# Viscometric Determination of Moisture in Honey

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EXPERIENCE has shown that, despite the fundamental accuracy of the vacuum-drying method (3) for the determination of moisture in honey, there is need for a rapid, accurate physical method to supplement it in routine testing. Studies have been made to meet this need by densimetric (7, 9), refractometric (4, 5, 8), and viscometric (8) means. The evident inaccuracies of the hydrometer, when used in highly viscous sirups, seemed to place the densimetric method outside the scope of the present investigation. Exploratory experiments made in this laboratory on a series of representative types showed a very poor degree of correlation between the refractive index of a honey and its moisture content as determined by the "official" procedure (3). Furthermore, many samples of this group were found to show such a blurred field in the Abbe refractometer as to render accurate readings impossible. The relative viscosities of these samples, on the other hand, showed a very high degree of correlation with their moisture contents. A thorough investigation of this phase of the problem was accordingly undertaken, and the results are summarized below.

## Design of Viscometer

Chataway (8) was apparently first to point out the correlation between the relative viscosity of honey, measured by the falling-sphere method, and its moisture content. According to her method for determining viscosity, a glass tube filled with honey is supported vertically in a jar of water until thermal equilibrium is established. A steel ball is introduced at the top and its time of fall determined as the ball travels the distance between two marks on the side of the tube. Tables are provided for translating the time of fall thus obtained into moisture content.

A comparison of Chataway's apparatus and method with those of other workers (6, 11) reveals the desirability of certain modifications. The most important of these are the substitution of the smallest commercially available (0.16-cm., 0.06-inch diameter) steel balls for the 0.475- and 0.23-cm. (0.19- and 0.094-inch) ball bearings employed by her, and the specification of 25-mm. standard-wall Pyrex tubing for the body of the viscometer, rather than the smaller size which was used by Chataway. These changes are vital because of the phenomenon of "wall effect." It was early recognized (14) that the time of axial fall of a sphere through a viscous medium in a vertical cylindrical tube is greater than that calculated by Stokes (17) for a sphere falling in an infinite medium, and that the amount of divergence, or wall effect, is a function of the ratio  $d/D$ , in which  $d$  and  $D$  are the diameters of the sphere and cylinder, respectively. Without going into the mathematical treatment of this phenomenon, it will suffice to emphasize that an easily reproducible falling-sphere viscometer must have a small wall effect, hence a small ratio  $d/D$ . This is true, because, although steel ball bearings may be easily duplicated within close limits of tolerance, glass tubing varies considerably from lot to lot, and it is important that such variations should not materially change the observed results. The effect upon time of fall of varying the diameter of the tube within wide limits is shown in Table I, due to Gibson and Jacobs (11).

These data were obtained using a 0.16-cm. (0.06-inch) ball falling through castor oil at 20° C., and it may be safely assumed that about the same degree of variation would be encountered in substituting honey for the oil. It may be fur-

ther assumed that the per cent variation in time of fall resulting from a fixed per cent variation in tube size depends only upon the values of the ratio  $d/D$  and not upon the actual values of either  $d$  or  $D$ ; in other words, that observations using a 0.15-cm. ball in a 2.1-cm. tube would be subject to

TABLE I. RELATION OF WALL EFFECT TO TIME OF FALL

Diameter of Tube	Time of Fall for 15 Cm.	$d/D$
Cm.	Sec.	
0.85	25.2	0.1870
1.14	21.8	0.1395
2.10	18.8	0.0757
3.50	17.7	0.0454
4.54	17.4	0.0350

the same percentage error as those using a 1.5-cm. ball in a 21-cm. tube, should each tube vary 1 per cent in diameter. If this be granted, then it can be shown graphically from these data that viscosity determinations using apparatus according to Chataway's specifications are subject to errors upwards of 8 per cent from the normal variations ( $\pm 0.5$  mm. in 25-mm. tubing) present in different lots of glass tubing, while the probable errors from the same cause, using the apparatus of Gibson and Jacobs (11), are of the order of 1 per cent.

Besides the indispensable factors just mentioned, several other desiderata enter into the design of a satisfactory falling-sphere viscometer. These are a means for

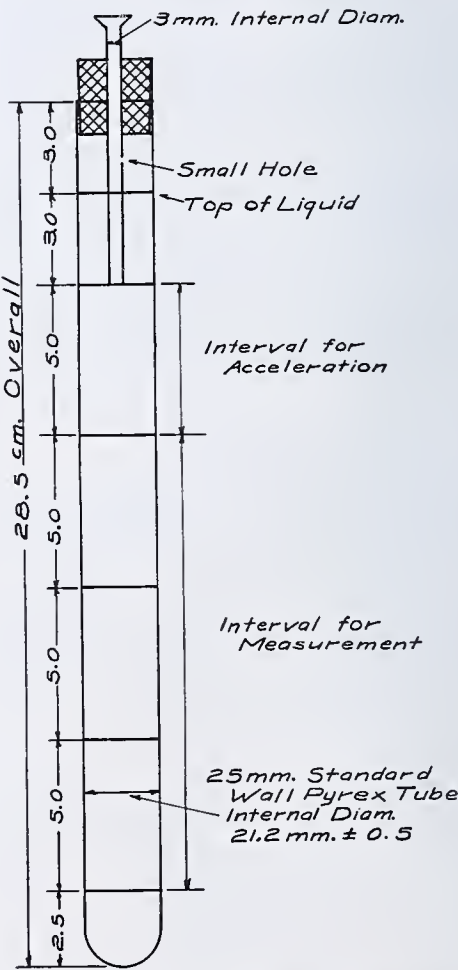


FIGURE 1. MODIFIED GIBSON-JACOBS VISCOMETER FOR DETERMINING MOISTURE CONTENT OF HONEY

freeing the sphere of entrained air bubbles, and for introducing it into the exact center of the tube, a fixed acceleration zone above the zone of measurement, wherein the sphere may acquire uniform velocity, and a constant height of liquid to eliminate the effect of hydrostatic pressure. The viscometer of Gibson and Jacobs (Figure 1) embodies these principles of design in simple, practical form, and was therefore adopted for use in this study. The calibration differs from that of Gibson and Jacobs (11) only in that the 15-cm. measuring zone is subdivided into three 5-cm. spaces.

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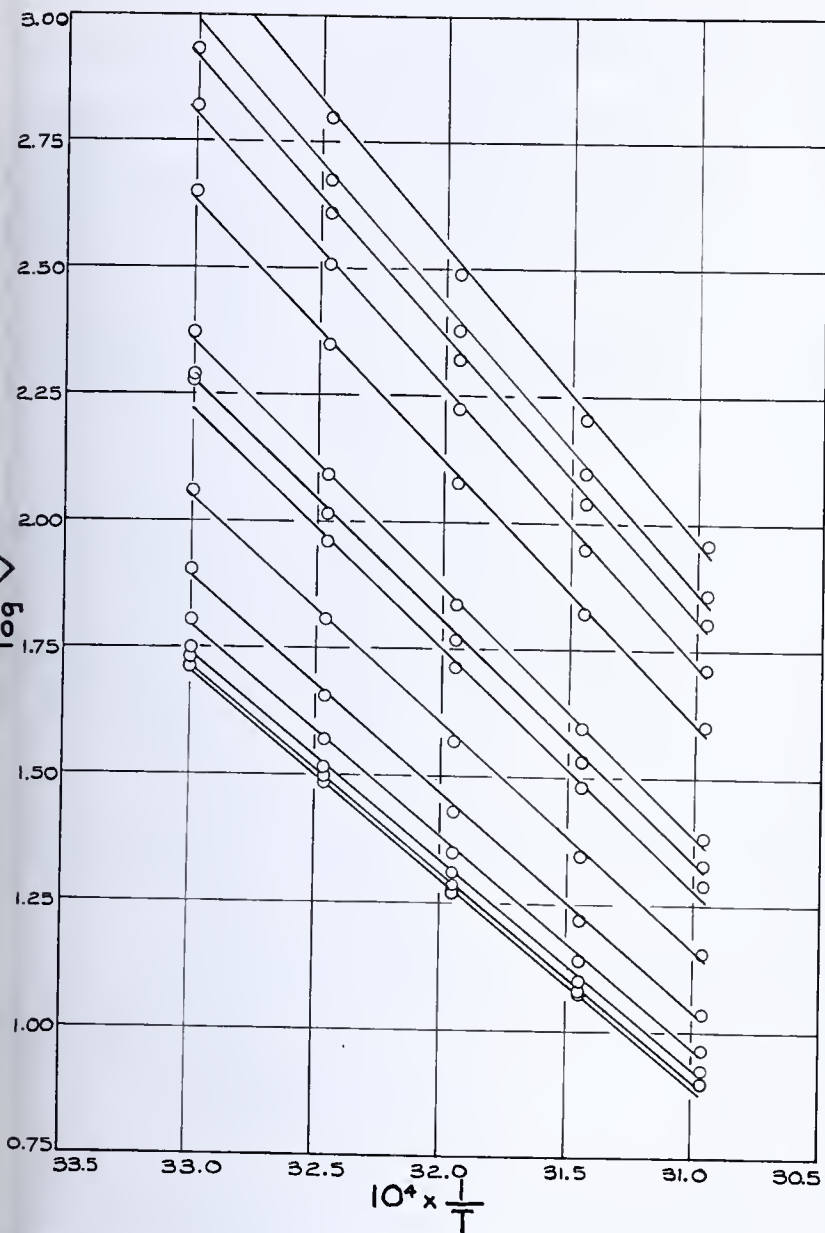


FIGURE 2. EFFECT OF TEMPERATURE UPON VISCOSITY OF INDIVIDUAL HONEYS

Accurate temperature control is essential to viscometric work, because viscosity is an exponential function of temperature. In fact, observations could not be duplicated unless the temperature remained within  $\pm 0.05^\circ$  of the recorded value.

Experimental Method

The apparatus consisted essentially of the tube, calibrated as described, mounted vertically in a metal frame. The frame and tube were placed in a diffusely illuminated glass constant-temperature bath, provided with a stirrer and surrounded by insulation, in which an observation window was cut. Following the procedure of Gibson and Jacobs (11), the steel balls were introduced below the surface of the honey through the 3-mm. tube. This served to free the ball of air bubbles and to ensure its fall through the center of the viscometer tube, thus eliminating two of the common sources of error alluded to above. Uniform height of column was maintained by filling the viscometer tube with the thoroughly liquefied and well-mixed honey sample exactly to the highest calibration, while uniform conditions of fall were assured by adjusting the end of the 3-mm. tube to the mark 6 cm. from the top. The 5-cm. portion immediately below served to allow the ball to acquire velocity, while the last 15 cm. marked were used for the actual readings. When working with very viscous samples it was possible to measure the time of fall through the first and third 5-cm. subdivisions of the measuring zone, and, multiplying each value by 3 to convert to the standard 15-cm. distance, to obtain two measurements with the same ball.

With this viscometer the relative viscosities (time of fall in seconds through 15 cm.) were determined for 15 honeys of widely varying moisture contents, at intervals of  $5^\circ$  from  $30^\circ$  to  $50^\circ$  C. As a result of this preliminary work,  $40^\circ$  was selected as a convenient standard temperature. A total of 30 honeys was measured at this temperature. Before making readings, samples were carefully mixed, and allowed to remain in the tube until all the bubbles in the body of the liquid had risen to the top. Thermal equilibrium was assumed to have been reached when close checks (about 0.4 per cent of the total time of fall of the sphere) were obtained several minutes apart. Concurrently, the moisture content of these samples was determined by the official vacuum drying method (3), cooling the dishes for 3 hours instead of the prescribed short time.

Mathematical Analysis of Results

The mathematical treatment of the data is a straight-forward application of elementary analytical geometry. Inasmuch as three interrelated variables are involved—moisture content,  $w$ , viscosity,  $V$ , and absolute temperature,  $T$ —the relation between any two is most conveniently ob-

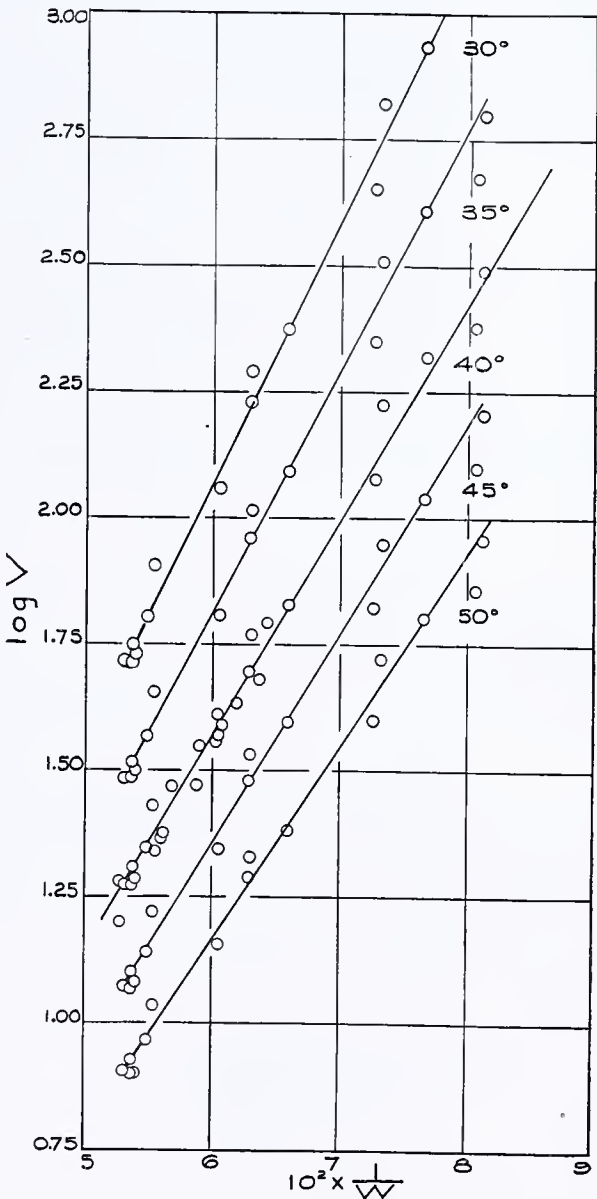


FIGURE 3. VARIATION OF VISCOSITY WITH MOISTURE CONTENT AT VARIOUS TEMPERATURES



served while holding the third constant. Two such relations are directly accessible as follows: (1) between viscosity and

temperature, with per cent moisture constant, and (2) between viscosity and per cent moisture at constant temperature.

Upon combination of these two relations, a general equation in  $w$ ,  $V_T$ , and  $T$  is obtained, from which  $w$  can be calculated for any values of  $V$  and  $T$ . This equation is an interesting and compact expression of the data reported, but becomes a bit awkward when applied to routine calculations. For this reason, a direct-reading graph was constructed which greatly simplifies the interpretation.

### Relation between Viscosity and Temperature with Per Cent Moisture Constant

It was hoped that the equation

$$\log V_T = a/T + b$$

where  $a$  and  $b$  are empirical constants, reported by numerous investigators (1, 2, 10, 12, 13, 15, 16), would hold. Although a slight curvature resulted, as is general for associated liquids, when  $\log V_T$  was plotted against  $10^4 \times 1/T$ , nevertheless, over the short range of temperature employed, the assumption of a straight-line function gave rise to errors considerably less than those due to other causes (Figure 2). The factor  $10^4$

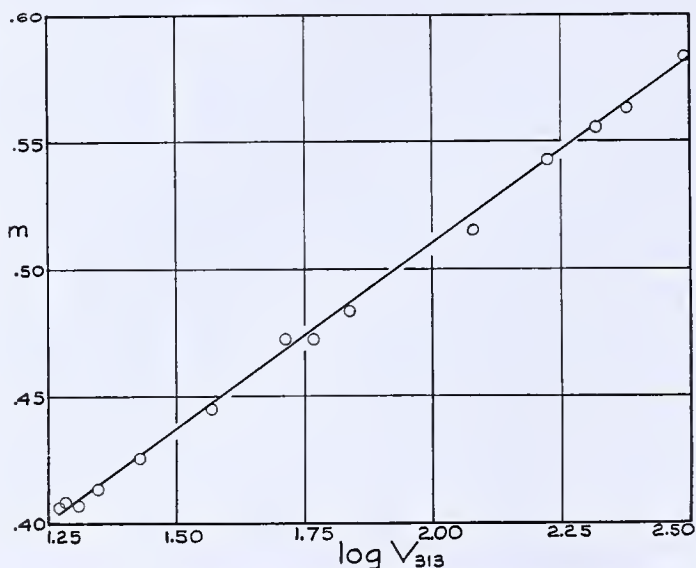


FIGURE 4. RELATION BETWEEN SLOPES OF FIGURE 2 AND VISCOSITY AT 40° C.

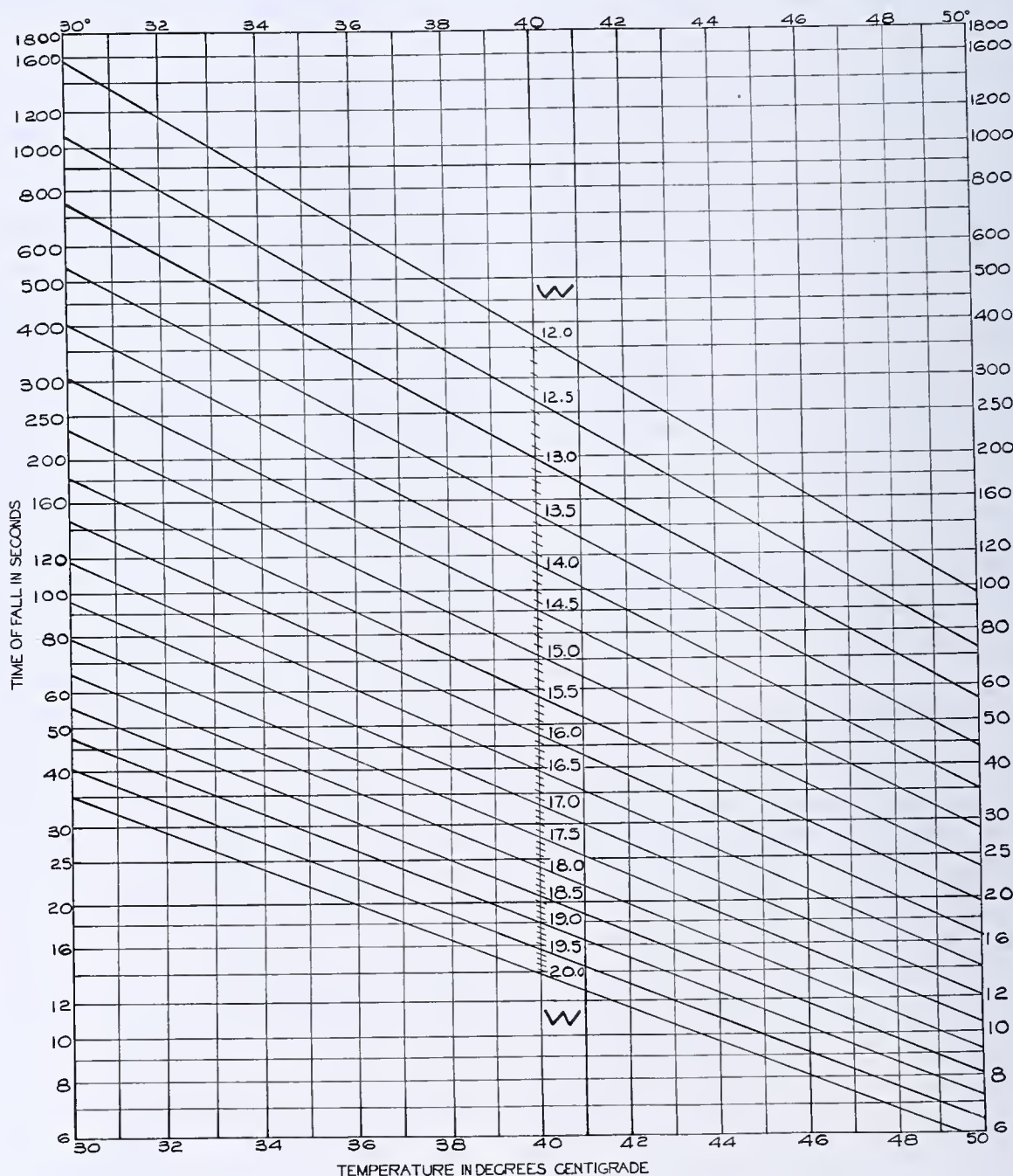


FIGURE 5. DIRECT-READING MOISTURE-VISCOSITY GRAPH



TABLE II. MOISTURE CONTENT OF HONEY

Sample	Viscosity, $V_{40}$ Sec.	Moisture Content		Difference
		By evapora- tion, official method	From viscos- ity, graphic method	
		%	%	%
1	37.0	16.52	16.7	+0.2
2	23.2	17.85	18.2	+0.3
3	36.0	16.59	16.8	+0.2
4	50.7	15.90	15.8	-0.1
5	68.1	15.16	15.2	0.0
6	26.9	18.05	17.6	-0.7
7	20.4	18.69	18.5	-0.1
8	19.3	18.52	18.8	+0.3
9	18.7	18.64	18.9	+0.3
10	47.9	15.70	16.0	+0.3
11	42.9	16.16	16.3	+0.1
12	32.8	16.46	16.6	+0.1
13	62.0	15.56	15.3	-0.3
14	238.5	12.39	12.7	+0.3
15	119.6	13.76	13.9	+0.1
16	22.3	18.21	18.3	+0.1
17	18.9	18.82	18.8	0.0
18	19.1	18.99	18.8	-0.2
19	35.4	16.96	16.8	-0.2
20	29.6	17.09	17.4	+0.3
21	21.8	18.02	18.3	+0.3
22	29.4	17.59	17.4	-0.2
23	15.8	19.73	19.5	-0.2
24	209.4	13.04	12.9	-0.1
25	310.3	12.31	12.3	0.0
26	58.6	15.86	15.5	-0.4
27	23.7	18.12	18.1	0.0
28	167.6	13.64	13.3	-0.3
29	40.8	16.56	16.4	-0.2

is introduced merely for convenience. This equation may be converted to the form

log  $V_T - \log V_{T_1} = m(1/T - 1/T_1)$  (1)

in which  $V_{T_1}$  is the viscosity at any particular temperature  $T_1$ , and  $m$  is the slope of the line. This may be rearranged, and adapted to the data of Figure 1 at 40°, by the introduction of the factor 10<sup>4</sup>, to yield

log  $V_{313} = \log V_T - \frac{313 - T}{0.0313 T} \times m$  (2)

From this can be calculated  $V_{313}$  (viscosity at 40°) knowing the viscosity at any other temperature—that is, Equation 2 can be used to correct the viscosity at any other temperature to 40°.

Relation between Viscosity and Moisture with Temperature Constant

Trial showed that the reciprocal of per cent moisture yielded a straight line when plotted against log  $V$  for any one temperature (Figure 3). Since 40° has been selected as the standard, it is only necessary to know the equation at this temperature for calculation of  $w$ , the per cent moisture, as values of  $V$  for any other temperature between 30° and 50° can be corrected to 40° with Equation 2. The viscosity-moisture equation at 40° was determined to be

log  $V_{313} = \frac{42.8(16.00 - w)}{16.00 w} + 1.676$  (3)

The correlation of points is not as good in Figure 3 as in Figure 2. This may be attributed both to the difficulty of obtaining uniform results with the A. O. A. C. method (3) and to the fundamental lack of a closer correlation between viscosity and moisture content.

General Relation of Viscosity-Moisture-Temperature

It was evident that Equations 2 and 3 would be more convenient if combined into one expression, because only one calculation would then be necessary for moisture determinations at temperatures other than 40°. This combination

was effected as follows: The slopes,  $m$ , of the family of straight lines in Figure 2 were determined graphically and plotted against the values of log  $V_{313}$ , corresponding to each value of  $m$ , resulting in the straight line of Figure 4. Its equation was determined to be

$m = 0.1460 \log V_{313} + 0.2175$  (4)

By substituting 4 in 2 and solving for  $V_{313}$  there is obtained

log  $V_{313} = \frac{(0.0313 \log V_T + 0.2175 T - 68.1)}{45.7 - 0.1147 T}$  (5)

Finally, by equating the values of log  $V_{313}$  given in 3 and 5 there results, upon solving for  $w$ , the equation

$w = \frac{62,500 - 156.7 T}{T (\log V_T + 1) - 2.287 (313 - T)}$  (6)

which gives  $w$ , as desired, in terms of  $V_T$  and  $T$ .

Graphic Representation of Equation 6

Because of the realization that the solution of Equation 6 might be an obstacle in practice, it was decided to represent the material contained therein graphically for rapid and convenient reference. Accordingly, Figure 5 was constructed, from calculated values of  $m$  and log  $V_{313}$  corresponding to even values of  $w$ , the scales being marked in terms of seconds, percentages, and Centigrade temperatures directly. In order to obtain the per cent moisture from this graph, it is necessary only to locate point  $p$  on the graph corresponding to the observed values of viscosity and temperature, and lay a straightedge through  $p$  in the mean direction of the adjacent "isomoisture" lines. At the point of intersection of the straightedge with the moisture scale, the per cent is read as closely as possible.

Summary

The relative viscosity, as measured by the falling-sphere method under vigorously defined conditions, affords a rapid and practical method of determining the moisture content of honey. The results may be evaluated either by the use of empirical equations or, more simply, by the use of a specially constructed graph. A comparison of the results (Table II) on 29 samples of honey of different floral types by the viscometric and official drying methods showed an average difference of 0.2 per cent.

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# Radiator Antifreeze Materials

## Identification in Used Crankcase Oils

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**D**URING the winter season complaints regarding motor oils increase, largely because of the accidental introduction into the crankcase of liquids used in the cooling system of the automobile rather than any inherent fault of the oil. Such liquids frequently consist of water and added antifreeze materials. Since the water which is found in a crankcase may have accumulated by condensation or because of a leak in the cooling system, merely identifying the water does not locate the engine condition to be rectified. If the radiator antifreeze material can be identified in the crankcase liquid it tells the automotive engineer that the cooling system needs overhauling. If no radiator liquid is present in the crankcase water, it may mean that the crankcase is operating at too low a temperature or that better crankcase ventilation should be provided.

Among substances found by the authors in used lubricating oils taken from the crankcases of cars experiencing trouble were methyl, ethyl, and isopropyl alcohols, glycerol, ethylene glycol, and calcium chloride. Each of these substances has likewise been found in radiator antifreeze solutions recommended to automobile users. Obviously, none can be considered a proper substitute for lubricating oil.

The method to be described has been found satisfactory for the detection of these antifreeze materials in used oils or deposits taken from automobile crankcases. By means of it as little as 0.2 per cent by volume of each liquid and 0.03 per cent by weight of calcium chloride in the oil has been definitely detected. The presence of any one compound alone did not cause a positive result to be obtained for any of the others nor did the simultaneous presence of all compounds interfere with the detection of any one. Since slight amounts of the lower alcohols can conceivably result by oxidation through normal use of the lubricating oil or engine fuel, uncertain tests for them should be considered negative.

### Separation of Liquids and Calcium Chloride

A well-mixed sample of the oil or deposit taken from the automobile crankcase is placed in a 500-ml. round-bottomed flask with 100 ml. of volatile petroleum solvent (commercial isooctane, 39 cents per gallon) and a few glass beads to prevent bumping. The apparatus is then assembled, heat applied, and the aqueous distillate collected for one hour. The general procedure is otherwise similar to the A. S. T. M. method (1) for water in petroleum products. The glass apparatus (Figure 1, A) has interchangeable ground joints. The special trap, which has a capacity of 25 ml., was furnished on order by the Ace Glass Co., Inc., Vineyard, N. J.

The sample taken should be large enough to yield at least 3 ml. of aqueous distillate. If the water content of the sample be very low, it is advisable to add 3.0 ml. of water to the sample before it is distilled, rather than use more than a 100-ml. sample.

At the end of one hour of distillation the heating is discontinued and the aqueous distillate is promptly withdrawn and retained for subsequent testing for methyl, ethyl, and isopropyl alcohols and ethylene glycol. When the apparatus has cooled the hydrocarbon distillate is withdrawn and discarded. The trap is then rinsed with 3 ml. of distilled water and the test for glycerol is subsequently made on these rinsings. The bulk of the glycerol that distills under these conditions adheres to the walls of the

A method is described for the identification of antifreeze materials in automobile crankcase oils where they occasionally find their way from radiators in winter service. It has been satisfactorily applied for the detection of calcium chloride, glycerol, ethylene glycol, and methyl, ethyl, and isopropyl alcohols.

trap, and has been consistently detectable. The residue left in the flask is tested for calcium chloride.

Substituting direct extraction with water for the distillation procedure as the means of obtaining the antifreeze liquids usually resulted in annoying emulsions, excessive dilutions, and conditions which caused glycerol to interfere with the glycol test. The distillation appears essential in the presence of glycerol, to preclude it from giving the glycol test.

### Detection of Calcium Chloride

To the flask containing the cool distillation residue add a few milliliters of distilled water, shake thoroughly, and allow to settle in a separatory funnel. Withdraw the aqueous layer through a wet filter paper and test one portion of it in the usual manner for chloride with silver nitrate solution, and another portion for calcium with ammoniacal ammonium oxalate.

### Detection of Antifreeze Liquids

**GLYCEROL.** Glycerol may be suspected if during the primary distillation the glass parts in the vapor space do not drain cleanly after one hour. For the detection of glycerol the method is essentially that of Mulliken (5), involving the dehydration of the alcohol with the formation of acrolein. The use of the smaller apparatus reduced the dead air space and increased the sensitivity of the test.

**Reagents.** Potassium bisulfate powder and concentrated hydrochloric acid.

Schiff reagent, prepared by dissolving 0.2 gram of rosaniline hydrochloride in 120 ml. of hot water. Cool, adding 2 grams of anhydrous sodium sulfite dissolved in 20 ml. of water, followed with 2 ml. of concentrated hydrochloric acid, and then diluting with water to 200 ml. The reagent is kept in a glass-stoppered bottle (amber colored).

**Procedure.** Place 1.0 ml. of the aqueous trap rinsings on a watch glass and heat it on a slow steam bath to evaporate the water. Absorb the residue left on the watch glass with about 0.5 ml. of powdered potassium bisulfate and transfer it to a 5-ml. flask. Attach the delivery tube and place its end under the surface of 0.5 ml. of distilled water in a small test tube (75 × 10 mm.) cooled by an ice-water bath (Figure 1, B). Heat the flask with flame, gently until frothing ceases and the mass fuses, and then more vigorously for a few minutes, including about three fourths of the neck as well as the bulb.

Remove the delivery tube, being careful to allow its liquid contents to run into the test tube. To this solution add 1 ml. of Schiff reagent, stopper, and shake well. A deep purple color will soon appear on standing and persist for many hours if glycerol was present. After standing for 24 hours the addition of an equal volume of concentrated hydrochloric acid causes the color to become a yellow-brown; if 2 ml. of this latter solution are then added to 30 ml. by slowly adding water, the color changes through green to blue or violet-blue.

This test was effective on the distillate obtained from oil containing less than 0.2 per cent of glycerol.

**ETHYLENE GLYCOL.** The presence of ethylene glycol is shown by the presence of oxalic acid after oxidation with nitric acid (4, 8).

**Reagents.** Concentrated nitric acid, concentrated ammonium hydroxide, and 10 per cent aqueous solution of calcium chloride.

**Procedure.** Into a test tube (22 × 200 mm.) introduce 0.5 ml. of the aqueous distillate and 3 ml. of distilled water. Keep the



test tube in a boiling water bath until the volume of solution has been reduced to 2 ml.; then add 2 ml. of concentrated nitric acid, transfer the solution to a 25-ml. Erlenmeyer flask, and boil it gently for 5 minutes but do not evaporate to dryness. The sample will give off brown fumes. Cool in ice and make alkaline by cautiously adding concentrated ammonium hydroxide from a dropper. Upon addition of the calcium chloride reagent, white calcium oxalate will be precipitated if ethylene glycol was present.

This test worked satisfactorily on the distillate obtained from oil containing as little as 0.1 per cent of ethylene glycol.

### General Test for Methyl, Ethyl, and Isopropyl Alcohols

The presence of the volatile alcohols, methyl, ethyl, and isopropyl, is shown by a general test. If the result be positive, a separate test for each alcohol is made by the specific methods which follow. A positive result by this general test is not final proof that a volatile alcohol is present because there are other substances which give the same reaction. However, a negative result indicates the absence of methyl, ethyl, and isopropyl alcohols.

Rosenheim (7) used a solution of ammonium thiocyanate in acetone or ethyl alcohol for the detection of cobalt salts. It

was expected that an aqueous solution of ammonium thiocyanate containing a cobalt salt would give the same reaction upon the addition of alcohol, but the authors found that a high concentration of ethyl alcohol (50 per cent minimum) was required to produce the color change, and they therefore developed the following scheme which permits the detection in low concentrations:

**REAGENTS.** Anhydrous sodium carbonate.

Cobaltous nitrate-ammonium thiocyanate reagent, prepared by dissolving 0.5 gram of cobaltous nitrate in 25 ml. of distilled water and adding it to a solution of 5 grams of ammonium thiocyanate in 25 ml. of distilled water.

**PROCEDURE.** Dip a piece of filter paper into the cobaltous nitrate-ammonium thiocyanate reagent. Place it between two pieces of dry filter paper and cut off a strip 10 cm. long and just wide enough to fit the 2.5-mm. bore of the reflux tube (Figure 1, C). Remove the outside pieces of paper and place the test strip in the reflux tube so that the bottom edge of the paper is about 4 cm. above the lower end of the tube.

When properly prepared the test strip is pink in color. It should not be allowed to dry completely because this alone may cause it to turn blue.

Fill the small 1.5-ml. flask three-quarters full with anhydrous sodium carbonate (about 1 gram) and allow 0.5 ml. of the aqueous distillate to drop on the dry salt. Attach the reflux tube containing the test strip and put the flask on an electric plate which is already hot. Use an improvised wire tripod to hold the flask upright on a piece of asbestos with a hole in its center (Figure 1, C).

Observe the test strip as the vapors rise slowly in the reflux tube. In the presence of a low-boiling alcohol the test strip will turn greenish blue as the first ring of rising vapors contacts it.

The color disappears as the vapors containing large amounts of water reach the strip. Regulate heating so that vapors do not accumulate in the reflux tube and fill its bore with condensate, because this will frequently be too low in alcohol content to give the test which requires a rather high concentration. The appropriate concentration is present in the first vapor ring, though not always in the condensed liquid.

The general volatile alcohol test gave positive results in aqueous distillates containing as little as 2 per cent of methyl, and 1 per cent of ethyl or isopropyl alcohols, equivalent to less than 0.1 per cent on the basis of the sample of crankcase oil.

If a positive test is obtained, the following specific tests are used.

### Methyl Alcohol

For the identification of methyl alcohol, a modification of the method of Georgia and Morales (3) proved satisfactory. Glycerol and glycol, however, interfere and must be removed by distillation if found by the previous tests. If neither glycerol nor glycol be present, the first distillation step described below is omitted and two 0.25-ml. portions of the aqueous distillate are used for the test instead of the 0.5-ml. portions specified in the procedure.

**REAGENTS.** Ethyl alcohol solution, 5 per cent aqueous.

Permanganate reagent, prepared by dissolving 3 grams of potassium per-

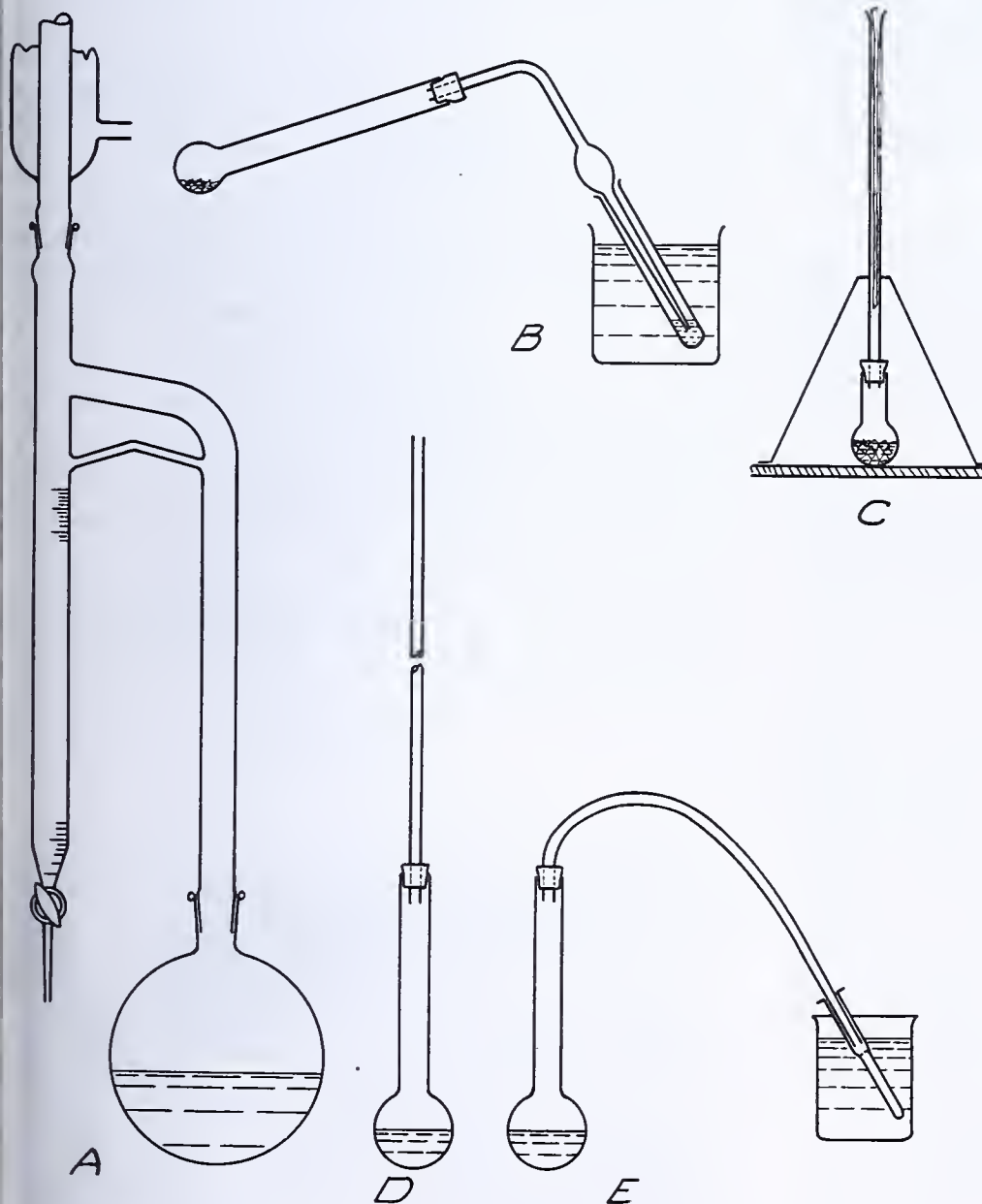


FIGURE 1. DIAGRAM OF APPARATUS

- A. Apparatus for separating liquid antifreeze compounds from oil sample  
 B. Apparatus for dehydration of glycerol and collection of acrolein  
 C. Apparatus used to detect presence of volatile alcohols  
 D, E. Apparatus for identification of isopropyl alcohol. D, Setup for digesting oxidation mixture, and E, Equipment for removing acetone produced by oxidation



manganate and 15 ml. of 85 per cent phosphoric acid in water and making up to 100 ml.

Oxalic acid reagent, prepared by dissolving 5 grams of oxalic acid in 100 ml. of dilute sulfuric acid (1 to 1).

Schiff reagent (as used for glycerol test above), pyrogallol, and concentrated sulfuric acid.

**PROCEDURE.** In a 15-ml. long-necked flask place 0.5 ml. of the aqueous distillate, 2 ml. of distilled water, and 1 or 2 pieces of Alundum to prevent bumping. Attach a delivery tube and very slowly distill off 1 ml. of liquid, collecting it in a 10-ml. graduate immersed in an ice-water bath. Divide this distillate into two equal parts and make the test for methyl alcohol in the following manner:

Place 5 ml. of the ethyl alcohol reagent in each of two test tubes. Add one portion of the distillate to the first test tube only, and 2 ml. of the permanganate reagent to each test tube. Stopper and shake thoroughly; then allow to stand for 10 minutes. Add 2 ml. of the oxalic acid reagent to each tube, mix again, and let stand until colorless. Add the second portion of distillate to the second test tube and add to each test tube 5 ml. of the Schiff reagent. Shake well, then allow to stand. A violet or blue color in the first tube and the absence of such color in the second test tube after standing 0.5 hour indicate the presence of methanol. If both tubes are colorless, methanol is absent.

If the second tube develops a blue or violet color, a new portion of the distillate should be treated to remove interfering aldehydes. To do this, introduce into a clean 15-ml. flask a solution of 0.2 gram of pyrogallol in 4 ml. of water, 0.5 ml. of distillate, and 1 ml. of concentrated sulfuric acid. Stopper and shake the flask; then allow it to stand for 10 minutes. If the mixture is pink, aldehyde is still present and more pyrogallol must be added to remove it. If the pink color is absent, distill off 2 ml. and test this distillate for methanol, using 1-ml. portions instead of the usual 0.5-ml.

This test was satisfactory in an aqueous distillate containing 1 per cent of methanol, equivalent to less than 0.1 per cent on the basis of the crankcase oil.

### Ethyl and Isopropyl Alcohols

These alcohols are detected by identifying the products which they form upon oxidation under controlled conditions. The isopropyl alcohol is oxidized to acetone, which is detected essentially by the method of Rae (6). The ethyl alcohol is oxidized to acetic acid and this is detected by a modification of the method of De Vito (2).

**ISOPROPYL ALCOHOL. Reagents.** Chromic acid solution. To 10 grams of chromium trioxide dissolved in 100 ml. of water slowly add, while stirring, 15 ml. of concentrated sulfuric acid.

Sodium nitroprusside solution. Add 5 ml. of aqueous 25 per cent sodium nitroprusside solution to 20 ml. of ammonium chloride solution containing 4 grams of ammonium chloride. This reagent should be freshly prepared.

Concentrated ammonium hydroxide.

**Procedure.** Into a 25-ml. flask introduce 10 ml. of chromic acid solution and a few pieces of Alundum to prevent bumping. Cool the flask in an ice-water bath, add 0.25 ml. of the sample to be tested, and attach a long reflux tube to the neck of the flask (Figure 1, D). Remove from the bath and allow the flask to stand at room temperature for 5 minutes. Then heat gently for 5 minutes, replace the reflux tube with a delivery tube (Figure 1, E), and finally collect 0.5 ml. of distillate and to this apply the following test for acetone (6), the oxidation product of isopropyl alcohol:

**Test for Acetone.** To 0.5 ml. of the sample in a small test tube (10 × 75 mm.), add an equal volume of sodium nitroprusside solution and mix thoroughly. Carefully overlay this mixture with about 1 ml. of concentrated ammonium hydroxide solution. A deep purple coloration appearing at the interface between the two liquid layers within 10 minutes shows the presence of acetone.

**ETHYL ALCOHOL. Reagents.** Chromic acid solution, prepared by dissolving 30 grams of chromic anhydride in 100 ml. of water and adding while stirring 40 ml. of concentrated sulfuric acid.

Sodium hydroxide solution, 0.1 N in water.

Dilute nitric acid, 1 volume of nitric acid to 9 volumes of water.

Lanthanum nitrate solution, 5 per cent in water.

Iodine solution, 0.1 N in aqueous 10 per cent potassium iodide.

Concentrated ammonium hydroxide.

**Procedure.** Into a test tube (22 × 100 mm.) introduce 5 ml. of chromic acid solution and 5 ml. of water. Bubble air through the liquid at a fairly rapid rate (45 liters per hour) and immerse the test tube in an ice-water bath. When the temperature drops to

10° C. or less, add to this solution 0.25 ml. of the sample at such a rate that the heat of reaction will not cause the temperature to rise above 30° C. After the reaction slows down and the temperature begins to drop, replace the ice bath by a warm water bath. Keep the temperature in the test tube at 35° ± 2° C. for 25 minutes, after which raise it to 60° ± 2° C. for a final 10-minute period. Five minutes after the 60° temperature has been reached, add 5 cc. more of chromic acid solution, taking care that the temperature remains within the required limits.

After the final heating stop the stream of air, transfer the solution to a 50-ml. distilling flask, and add 10 ml. of water to it, together with a few pieces of Alundum to prevent bumping. Heat the flask and collect the distillate in a long-necked flask (25 ml.) immersed in a beaker of ice and water. Continue the distillation until crystals appear in the distilling flask. Make the distillate alkaline with 0.1 N sodium hydroxide solution and evaporate to dryness on the steam bath in a 50-ml. beaker. Dissolve the residue in 1 ml. of water, add dilute nitric acid until the solution is decidedly acid, then divide this solution into 2 parts. Transfer one 0.5-ml. portion to a small test tube and test for acetic acid, the oxidation product of ethyl alcohol. Dilute the other portion with 2 volumes of water and test 0.5 ml. of this solution for acetic acid in the same manner, for confirmation.

**Test for Acetic Acid (2).** Introduce 0.5 ml. of the solution into a 10 × 75 mm. test tube and add an equal volume of lanthanum nitrate solution. Then add a drop of 0.1 N iodine solution and thoroughly mix the contents of the test tube. Carefully overlay this solution with about 1 ml. of concentrated ammonium hydroxide and allow to stand for 10 minutes. A deep blue or purple colored precipitate at the junction of the two liquids shows the presence of acetic acid.

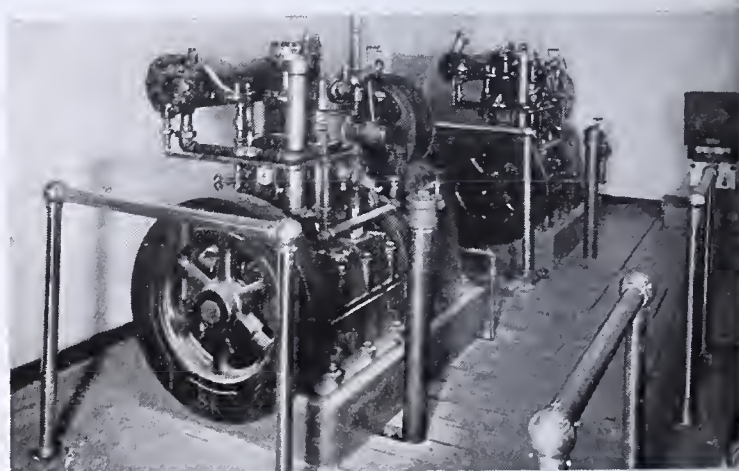
The tests for methyl, ethyl, and isopropyl alcohols and glycerol can be applied directly to any combination of these substances as a general analytical scheme. The presence of water or ethylene glycol does not interfere.

In an isolated case the authors found a sugar solution (apparently from use as a radiator antifreeze) in an automobile crankcase. Because it was an isolated case it does not seem necessary to include the method for its identification in this scheme.

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HELIUM AND HYDROGEN COMPRESSORS



# Volumetric Determination of Aluminum Using Sodium Citrate

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IT HAS long been recognized that the aluminum ion will react in the cold with excess of alkali citrate to liberate two hydrogen ions for each aluminum ion. In the presence of the citrate the liberated acid is conveniently titratable. With an alkali tartrate the aluminum ion in the cold liberates three hydrogen ions, the number ultimately formed on complete hydrolysis of the aluminum in water. It is difficult to titrate the acid liberated during normal hydrolysis, even though the added base tends to cause completion of the hydrolysis, but very easy to titrate the acid liberated in the presence of the tartrate. Thus White (4) many years ago outlined a method for the volumetric determination of aluminum in its sulfate by the utilization of both these organic salts, and successfully applied it to acidic and basic sulfates.

He found that barium hydroxide was better than sodium hydroxide as a standard solution for titrating the liberated acid. This base was standardized against sulfuric acid which contained approximately enough dissolved precipitated aluminum hydroxide to duplicate the conditions in samples being analyzed, thus eliminating a slight overtitration otherwise obtained in the "citrate step" outlined below.

Starting with 3 grams of aluminum sulfate dissolved in 100 cc. of water, two 25-cc. samples were removed for titration. To the first was added a 50-cc. portion of neutral 10 per cent potassium sodium tartrate. It was then titrated with the barium hydroxide to the phenolphthalein end point, thus neutralizing the acid equivalent to three times the number of moles of aluminum ion as well as any free acid. If free base was present, the volume used to titrate the liberated acid was diminished by an amount of base equivalent to the free base.

The second 25-cc. portion was evaporated to dryness, dissolved in 50 cc. of neutral 10 per cent sodium citrate solution, and after being allowed to stand 10 minutes was titrated cold with the base to the phenolphthalein end point. The amount of base used here was equivalent to the acid formed in the liberation of two hydrogen ions for each ion of aluminum, plus the free acid or minus the acid equivalent to the free base. Simple calculation enabled the amount of aluminum to be determined, along with the amount of free acid or free base present. Thus the aluminum itself was determined by multiplying the volume difference between the two titrations by three and then calculating the amount present by appropriate use of the molarity of the base. The alkaline earth sulfate did not immediately precipitate under the conditions of the experiment.

A study of White's work (4) indicated that the mole ratio of citrate to aluminum ion was somewhere between 3.2 and 8.6, depending on the states of hydration of his compounds, which were not definitely given. Evaporating the second portion to dryness gave results which otherwise could be attained only after the solution containing these substances had stood for many hours.

Recently Pavlinova (3) showed that thymolphthalein was a better indicator than phenolphthalein, for the titration of the acid liberated during the reaction of citrate with aluminum ion, since phenolphthalein changed color too quickly and thus gave a negative error. Using potassium aluminum sulfate of known molarity, she first titrated sodium citrate with sodium hydroxide to the thymolphthalein end point, then added the alum solution, and again titrated in the cold until the indicator changed color. As long as the mole ratio for citrate to aluminum ion was not much less than 1.2, and up to at least a ratio of 4.1, two hydrogen ions were liberated for each one of aluminum.

She also found that neutral solutions resulting from the titrations became basic upon boiling and then cooling, which showed that less acid would be liberated were this heat treatment applied to the original citrate-alum solution before titration. On the other hand with a very small ratio the neutral solutions became somewhat acidic on heating. No attempt was made to plot the liberated acid accurately against the mole ratio for citrate to aluminum in experiments in which heat treatment occurred, although it was obvious to the investigator that the curve would have an interesting course. Different temperatures also had different effects. She found it necessary to add phenolphthalein to the thymolphthalein in the experiments in which heating took place, since heat affected the latter.

In the authors' preliminary studies with the citrate-aluminum reaction equilibrium was slow to be attained in the cold, but heating caused it to be realized quickly. For this reason they made no attempt to evolve an aluminum method in which heating did not have a place.

## Variation in the Mole Ratio of Citrate to Aluminum

In deciding the amount of sodium citrate to be added, the effects of varying amounts upon a constant amount of aluminum were studied. The citrate-aluminum solution was first heated and then cooled before the liberated acid was titrated with sodium hydroxide. In these experiments the general method given below was followed except as to the amount of citrate used, starting where portion II is treated. The results indicated that the mole ratio of citrate to aluminum should be kept within certain limits in the general method, since one could no longer rely on the liberation of just two moles of hydrogen ion for each mole of aluminum ion. The heating had destroyed this simple relationship, although in the authors' opinion the gain in speed in attainment of equilibrium compensated for this.

Using 3.35 millimoles of aluminum as the sulfate, the amount of citrate was increased to more than 90 millimoles in experiments in which the liberated acid was titrated with 0.496 molar sodium hydroxide. The mole ratio of citrate to aluminum thus varied from much less than 1 up to more than 26. Complete hydrolysis of the aluminum would give 10.05 millimoles of hydrogen ion, which would be neutralizable by 20.26 ml. of the standard base. On the other hand the liberation of two hydrogen ions for each one of aluminum would result in the use of only 13.51 ml. of base.

With the small ratio of citrate to aluminum consequent upon the use of the smallest quantities of added citrate, the liberated acid approached the more than 20 ml. expected from complete hydrolysis, but as the mole ratio approached 1.2, the lowest value in the work of Pavlinova (3), there was a steep drop to a little over 50 per cent of that expected from complete hydrolysis. This value was less than the 66.7 per cent expected by the "cold method" of Pavlinova (3), or the method of White (4). Qualitatively Pavlinova had predicted such results but had not shown the exact influence of variation in added citrate.

The curve representing volumes of sodium hydroxide used, as ordinates, plotted against mole ratios of citrate to aluminum ion, as abscissas, kept on descending until a value of



about 45 per cent of the acid expected from complete hydrolysis in the absence of citrate was obtained. At this stage the mole ratio was 1.7 and about 9.3 ml. of the base were needed. The curve then rose and from a ratio of about 3 to about 11 it was a straight line with a steep slope. From a ratio of 15 to 26 only two or three points were obtained, but the curve was almost horizontal in this region and appeared to be straight again. Here the liberated acid amounted to close to two hydrogen ions for each aluminum ion and thus for the first time the results remained, over a long range, similar to those of the earlier workers with their different experimental conditions. The authors' "hot method" gave similar results when they used a ratio of 15 to 26, while Pavlinova (3) had used 1.2 to 4.1 with her cold method, and White (4) had utilized a ratio somewhere between 3.2 and 8.6, using a still different variation. White used the liberation of acid by the citrate as only part of his general method, but nevertheless relied on liberation of exactly two hydrogen ions for each aluminum ion.

The authors deemed it unwise to attempt to establish a method that required such a large amount of citrate as needed with a ratio of 15 or more for citrate to aluminum ion. It was decided that further studies could profitably be made in the region lying between ratios 3 and 11, where the rapidly ascending curve formed a straight line. Here the effect of the citrate on a given amount of aluminum was variable but was proportional to the amount of citrate present and so to the mole ratio of citrate to aluminum.

By using a constant amount of citrate and varying the aluminum, keeping the mole ratio within the above limits, and titrating the liberated acid another straight-line curve could be obtained when the base used in the titrations was plotted, as ordinate, against the amount of aluminum present.

### Establishment of Aluminum Method

It was necessary to select an appropriate amount of sodium citrate for addition to the aluminum in all cases. Since less than two ions of hydrogen were liberated for each one of aluminum, an equation was evolved for calculating the amount of aluminum in the sulfate from the amount of base used in titrating the acid liberated. A slightly different equation was necessary with potassium aluminum sulfate, because of the influence of the potassium ion. Confirmation of this effect of potassium was qualitatively obtained by tests in which potassium chloride was added in varying amounts to aluminum sulfate samples, with consequent increase in titratable acid with constant amount of citrate and aluminum. Sodium chloride did not have this important effect on the acidity.

The two equations were obtained by study of the curves made by plotting the base used against the aluminum present in the aluminum sulfate and the potassium aluminum sulfate.

### Reagents and Apparatus

Ordinary distilled water was used. Reagent solutions were properly protected from carbon dioxide after being made up. Since the presence of carbonate in the sodium hydroxide did not matter in this work, it was desired only to avoid further absorption in the standardized solutions.

Sodium hydroxide, 0.5 molar, was always standardized against two different samples of standard hydrochloric acid made up from separate sources of the constant-boiling acid.

Sodium citrate, 0.610 molar, was made from freshly opened sodium citrate dihydrate which contained 11.8 per cent of water, according to a private communication from the manufacturers. This U. S. P. product was later found to be definitely acidic to the authors' indicator when 4.7 grams were dissolved in a total volume of 100 ml. Under these conditions there was not over the equivalent of 0.06 ml. of 0.5 molar sodium hydroxide of ti-

tratable acid. Titration was made in the cold, without previous heating.

In making up sodium citrate solutions any sample not departing from the U. S. P. specifications of 10 to 13 per cent of water is satisfactory, since an error of 2 per cent in the amount of citrate used is inappreciable. The theoretical water content is 12.25 per cent for the dihydrate. If the sample departs from the acidity specifications outlined above, correction must be made by adding sodium hydroxide or sulfuric acid. The authors added 1 ml. of carbon tetrachloride to each liter of solution for preservative.

Aluminum sulfate,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , was dissolved, filtered, and found gravimetrically to contain 0.1815 mole per liter. This solution was used during tests in which the correction for free acid was made and thus added acid was tested for in various samples and satisfactorily recovered. Any free acid present in the sample itself would thus have been detected.

Potassium aluminum sulfate, c. p., was found gravimetrically to be 0.1776 molar.

Potassium fluoride. Reagent quality material was used.

Sulfuric acid was 0.5 *N* and was standardized against the sodium hydroxide. It was used, with the potassium fluoride, during tests on the procedure accorded portion I in the general method.

Indicator solution. After exhaustive tests on various indicators present during electrometric titrations 0.075 per cent thymolphthalein and 0.025 per cent phenolphthalein by weight, in alcohol, were selected as indicator. Fifteen drops were used in the 100-ml. total volume and the "colorless to rose" indication was used.

### Determination of Aluminum in Absence of Iron

Sodium hydroxide containing carbonate may be used except when solutions are to be heated. Thus in establishing this method and applying it to neutral aluminum solutions, it is not necessary to free the base from carbonate before standardization. Decidedly acidic solutions require adding a large corrective volume of base to portion II after making the determination in portion I. If this base contains carbonate, error is involved in heating portion II containing the added base. On the other hand adding the base after cooling the solution means heating the solution in the presence of the original free acid. With large amounts of free acid this is not permissible, as it would cause a shift in the end point of the ensuing titration. Thus with large amounts of free acid, and perhaps even with very small amounts, the corrective base in portion II must be added before heating and for this reason carbonate-free base is essential. Carbonate present in the sodium hydroxide will not cause error in the absence of free acid, and may cause no appreciable error with only fairly small amounts, provided the base is added after and not before heating.

**GENERAL METHOD.** Start with an iron-free sample containing between 80 and 430 mg. of aluminum (150 and 810 mg. of the oxide), and make up to 50 ml. in a volumetric flask. Remove 25 ml. with a pipet and use as portion I. Quantitatively transfer the remainder to another vessel as portion II.

Portion I. To find the correction for free acid add 6 grams of potassium fluoride, titrate with standard 0.5 *N* carbonate-free sodium hydroxide to the phenolphthalein end point, and discard the sample. [The treatment accorded portion I was based on the slightly modified method of Craig (1, 2). Tests made with the aluminum sulfate solution containing added sulfuric acid were satisfactory, in that the added acid was recovered. None of the solutions included in Tables I, II, and III were treated in this way, as simple aluminum salts were used in establishing and testing the method and the alum solution was made from c. p. material while the aluminum sulfate solution was indirectly tested as directed above (see also "Reagents and Apparatus"). The use of phenolphthalein in portion I, where a few drops of 0.1 per cent indicator were used, is defensible, since here one is not titrating acid liberated from the reaction forming the citrate-aluminum complex. The mixed indicator should be as good as or better than the phenolphthalein here, unless it is harder to get a sharp end point.]

Portion II. Add 25 ml. of 0.610 molar sodium citrate (see "Reagents and Apparatus," discussion concerning making up and



testing citrate). Dilute to nearly 100 ml., add the volume of sodium hydroxide used for portion I, bring the volume to 100 ml., and heat at the boiling point for 5 minutes. Cool, and titrate to a light color with the base, using the thymolphthalein-phenolphthalein indicator previously described. (The base need not be carbonate-free where there is no free acid correction.)

METHODS OF CALCULATION FOR ALUMINUM PRESENT IN PORTION II. For pure aluminum salts (potassium absent),

$$\text{Millimoles of Al} = \text{millimoles of NaOH} \times 0.697 - 0.341 \quad (1)$$

For potassium aluminum sulfate,

$$\text{Millimoles of Al} = \text{millimoles of NaOH} \times 0.674 - 0.317 \quad (2)$$

In each case millimoles of aluminum may be converted to milligrams of aluminum oxide by multiplying by 50.97.

TABLE I. DATA FOR EQUATION USED FOR ALUMINUM SULFATE SOLUTIONS

(Equation 1 is derived from these data)

NaOH = 0.494 molar.  $\text{Al}_2(\text{SO}_4)_3 = 0.1815$  molar

Corrected NaOH ML.	Volume <sup>a</sup> $\text{Al}_2(\text{SO}_4)_3$ ML.	NaOH Moles $\times 10^3$	Al Mg.	$\text{Al}_2\text{O}_3$ Mg.	Al Calcd. Moles $\times 10^3$	Deviation of Calcd. from Known Al %
2.88 ( $\pm 0.02$ )	2.01 ( $\pm 0.01$ )	1.423	0.730	37.2	0.651	-10.8
6.29 ( $\pm 0.04$ )	5.01 ( $\pm 0.03$ )	3.107	1.819	92.7	1.825	+ 0.3
11.58 ( $\pm 0.08$ )	10.03 ( $\pm 0.03$ )	5.721	3.641	185.6	3.647	+ 0.2
16.87 ( $\pm 0.07$ )	15.02 ( $\pm 0.07$ )	8.334	5.452	277.9	5.468	+ 0.3
22.26 ( $\pm 0.02$ )	20.05 ( $\pm 0.02$ )	10.997	7.278	371.0	7.324	+ 0.6

<sup>a</sup> Four runs made in each case.

ESTABLISHING CURVES FROM WHICH EQUATIONS WERE DERIVED. Simple aluminum salts were used in establishing the curves from which Equations 1 and 2 were derived. The authors began where portion II is treated in the general method, since corrections for free acid were superfluous.

TABLE II. DATA FOR EQUATION USED FOR POTASSIUM ALUMINUM SULFATE SOLUTIONS

(Equation 2 is derived from these data)

NaOH = 0.494 molar.  $\text{KAl}(\text{SO}_4)_2 = 0.1776$  molar

Corrected NaOH ML.	Volume <sup>a</sup> $\text{KAl}(\text{SO}_4)_2$ ML.	NaOH Moles $\times 10^3$	Al Mg.	$\text{Al}_2\text{O}_3$ Mg.	Al Calcd. Moles $\times 10^3$	Deviation of Calcd. from Known Al %
1.63 ( $\pm 0.01$ )	2.01 ( $\pm 0.01$ )	0.805	0.357	18.20	0.226	-37
3.48 ( $\pm 0.02$ )	5.01 ( $\pm 0.03$ )	1.719	0.890	45.36	0.842	- 5.4
6.25 ( $\pm 0.04$ )	10.03 ( $\pm 0.03$ )	3.088	1.781	90.78	1.764	- 1.0
8.94 ( $\pm 0.05$ )	15.02 ( $\pm 0.07$ )	4.416	2.668	136.0	2.659	- 0.3
11.61 ( $\pm 0.03$ )	20.05 ( $\pm 0.02$ )	5.735	3.561	181.5	3.548	- 0.4
14.33 ( $\pm 0.08$ ) <sup>b</sup>	25.07 ( $\pm 0.07$ ) <sup>b</sup>	7.079	4.452	226.9	4.454	0.0
17.07 ( $\pm 0.02$ )	30.05 ( $\pm 0.00$ )	8.433	5.337	272.0	5.367	+ 0.6
19.79 ( $\pm 0.05$ )	35.13 ( $\pm 0.00$ )	9.776	6.239	318.0	6.272	+ 0.5

<sup>a</sup> Four runs made.

<sup>b</sup> Discarded a value 14.53 corresponding to 25.07 in the next column, so only 3 runs.

The first five columns of Tables I and II contain the data used in plotting the curves for aluminum sulfate and potassium aluminum sulfate. The equations derived from the curves may be used in calculating the aluminum content of unknown solutions which are free from iron or from other interfering ions which liberate acid from citrate. In each table the numbers within parentheses refer to the maximum deviations of the volumes in individual runs from the average volumes given.

ADEQUACY OF EQUATIONS. In view of the fact that the data given are not shown in the form of the curves actually used, it seemed well to present in tabular form figures to show just how well the equations fit the data from which they were derived. Thus the last columns of Tables I and II present a comparison of the amounts of aluminum actually present with the amounts calculated by application of the equations. The percentage deviation is a measure of the adequacy of the equations, which are those fitting straight lines. This deviation, presented in the last column, indicates that over a long range the equations are applicable but that with smaller values for aluminum oxide they do not apply.

## Discussion

A sufficient test of the method of analysis, including the validity of the equations, is given above. The further test on aluminum sulfate merely confirms the finding for that material previously presented.

This is essentially a repetition of the type of work used to obtain the original equation for aluminum sulfate. Equation 1 is used in calculating the aluminum in solutions to which known amounts of aluminum have been added. The calculated values are then compared with the known values as was done in Tables I and II. In Table III the last column presents the percentage error of the calculated values obtained from the results of titrations when compared to the known aluminum content. Again the authors began work where portion II is treated, since the same aluminum sulfate solution was used as in the previous work.

TABLE III. TESTING METHOD OF ANALYSIS WITH ALUMINUM SULFATE

(Equation 1 is used)

Run No.	NaOH = 0.494 molar. $\text{Al}_2(\text{SO}_4)_3 = 0.1818$ molar		NaOH Moles $\times 10^3$	Al		Error %
	Corrected NaOH ML.	Volumes $\text{Al}_2(\text{SO}_4)_3$ ML.		Found Moles $\times 10^3$	Contained Moles $\times 10^3$	
1	2.88	2.01	1.423	0.651	0.730	-10.8
2	2.89	2.01	1.428	0.654	0.730	-10.4
3	2.86	2.01	1.413	0.644	0.730	-11.8
4	2.89	2.00	1.428	0.654	0.726	- 9.9
5	6.39	5.04	3.157	1.859	1.830	+ 1.6
6	6.44	5.01	3.181	1.876	1.819	+ 3.1
7	6.29	5.01	3.107	1.825	1.819	+ 0.3
8	6.25	4.98	3.088	1.811	1.808	+ 0.2
9	11.63	10.05	5.745	3.663	3.648	+ 0.4
10	11.59	10.00	5.725	3.649	3.630	+ 0.5
11	11.58	10.04	5.721	3.647	3.644	+ 0.1
12	11.54	10.03	5.701	3.633	3.641	- 0.2
13	16.94	15.06	8.368	5.491	5.467	+ 0.4
14	17.01	14.97	8.403	5.516	5.434	+ 1.5
15	16.84	15.09	8.319	5.457	5.478	- 0.4
16	16.91	14.96	8.354	5.482	5.430	+ 1.0
17	21.18	19.07	10.463	6.952	6.922	+ 0.4
18	22.24	20.07	10.987	7.317	7.285	+ 0.4
19	23.21	21.06	11.466	7.651	6.645	+ 0.1
20	24.09	22.06	11.900	7.953	8.008	- 0.7

From the plotted data of all three tables the limits of applicability of the method were derived. The general method may be considered precise to 1 per cent over the region advocated for its use, which is between 150 and 810 mg. of aluminum oxide in the whole sample, or half of these values in the part used as portion II. As variations within the prescribed limits of the acidity of the citrate used may account for 1.1 mg. possible error in evaluating the amount of oxide in an unknown, even the smaller samples used in portion II will be essentially within this precision limit.

## Conclusion

While sodium citrate is an essential reagent in an excellent volumetric aluminum method developed long ago, and is also used in a more recent cold method, the authors were not satisfied that equilibrium was attained quickly enough without heating. Their method involves a correction for any free



acid, and the cold titration of the acid liberated from a previously heated mixture of sodium citrate solution with the unknown aluminum solution. The calculation of the aluminum content is based on substitution in an appropriate equation of the amount of sodium hydroxide used in titrating the liberated acid. The method is applicable to solutions which are free from appreciable quantities of iron or other interfering ions.

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# Pycnometric Determination of Lead as Sulfate

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**The new method in pycnometric analysis has been adapted to the determination of lead as sulfate in two nonferrous alloys with satisfactory results. The behavior of the lead sulfate precipitate is such that centrifugalization can be eliminated, thereby considerably simplifying the method.**

IN A RECENT preliminary report (3) upon a new method in pycnometric analysis, its underlying theory and probable accuracy were discussed, and pycnometric analyses were presented for the barium, iron, or silver in several simple substances, primarily salts. The present work deals with practical analyses of two nonferrous alloys of widely different lead contents. The lead was determined as sulfate because this is the compound most frequently used for its separation and gravimetric determination. The relatively high density of lead sulfate is an asset in the pycnometric method, while its solubility offered an opportunity to apply the pycnometric method to a precipitate of considerably greater solubility than any studied previously in this laboratory.

## Density of Lead Sulfate

Inasmuch as a pycnometric analysis actually determines the volume of a precipitate, the weight can be ascertained only if the density of the precipitate, or strictly speaking the apparent density characteristic of the experimental conditions existing during the analysis, is accurately known. Other things being equal, the more soluble the precipitate, the greater will be the difference between its absolute and apparent density. In order to determine the apparent density of lead sulfate, a primary standard of accurately known lead content must be subjected to the pycnometric procedure which is to be used subsequently in the analysis. The principal primary standard used in the present work was the Bureau of Standards lead block, No. 49, melting point 327.3° C. The results of nine determinations, leading to an average value of 5.791, are given in Table I. This value is to be used in computations of analyses in which 3 per cent sulfuric acid is used as the standard washing medium in approximately the amount and manner specified below.

The values for the density of lead sulfate given in the literature show a considerable variation. The numerous values listed in Mellor (2) vary from 5.97 to 6.393, while the value given in the International Critical Tables is 6.2. Furthermore, Krings (1) found that lead sulfate formed in

aqueous solution has a lower density (6.03), than that formed by fuming with sulfuric acid (6.272), and that ignited lead sulfate has a lower density than the freshly prepared precipitate. A comparison of the apparent with the real density of lead sulfate therefore required a determination of the latter value for the lead sulfate precipitate formed under the conditions of the analyses. The lead sulfate precipitates in the present work redissolved in the strong sulfuric acid during the fuming and were formed again upon dilution with water. In six density determinations values of 6.309, 6.277, 6.290, 6.298, 6.338, and 6.292 were obtained, leading to a mean value of 6.301 for the real density of the lead sulfate precipitate. Thus, the real density of the lead sulfate precipitates in the present work is 6.301 while the apparent density when using 3 per cent sulfuric acid is 5.791. The densities of the sulfuric acid used in the present work varied between 1.02475 and 1.0351 at 30° C.

## Apparatus

The apparatus employed was essentially the same as that already described (3). Most of the work has been carried out with 1-cc. pycnometers, although 3-cc. pycnometers were occasionally used. In the latter part of the work the hand-made pycnometers were replaced by vessels of similar design provided with precision ground-glass joints of standard taper (made by the Scientific Glass Apparatus Company, Bloomfield, N. J.) which have proved very satisfactory.

The evaporation of liquid from the precipitation flasks can be efficiently conducted by surrounding the vessel with a close-fitting conical asbestos paper hood, which is readily molded from wet asbestos paper and holds its shape after baking. It is held in position around the flask by a separate, split collar of asbestos paper which is kept firmly in place around the narrow flask neck by a twist of wire. These hoods are readily slipped on and off the precipitation flasks as required.

## Method

The analytical procedure is in general similar to that already described (3). Since the alloys analyzed contain tin

TABLE I. APPARENT DENSITY OF LEAD SULFATE

Weight of Lead Block 49 Gram	Apparent Density at 30° Grams/cc.
0.20735	5.746
0.2079	5.827
0.20835	5.771
0.20905	5.832
0.2002	5.807
0.4998	5.778
0.50045	5.785
0.19945	5.778
0.19985	5.791
	Av. 5.791



and antimony, these elements are first removed in the customary manner.

The weighed sample is dissolved in a mixture of 15 cc. of concentrated nitric acid and 10 cc. of water and evaporated in the course of an hour to 5 to 10 cc. on a steam bath. After adding 10 cc. of water the precipitate is digested on a steam bath for 5 to 20 minutes. The precipitate containing tin and antimony, well mixed with paper pulp, is filtered off and well washed with 5 per cent nitric acid. The combined filtrate and washings, having a volume of about 400 cc., are evaporated to about 10 cc. and then rinsed in a 125-cc. precipitation flask with 20 to 30 cc. of 5 per cent nitric acid. For evaporations the precipitation flask should not contain more than 30 to 40 cc. of liquid.

An asbestos hood is now placed around the precipitation flask, and its contents are evaporated to about 10 cc. on a hot plate. With the asbestos hood in place the solution boils quietly without bumping. To the cold solution 20 cc. of concentrated sulfuric acid are now added and evaporation is continued on the hot plate to copious fumes of sulfur trioxide. By proper regulation of the hot-plate temperature this operation also occurs quietly without bumping. The precipitate of lead sulfate dissolves shortly before the end of the fuming operation. To the cold clear concentrated acid solution, 80 cc. of water are added, introducing the first portions very cautiously with good agitation. The mixture is digested for at least an hour on the steam bath to ensure a uniformly coarse precipitate.

After digestion the solution is cooled and the precipitate settled while the precipitation flask is left in an inclined position. When then the flask is carefully placed in the upright position the precipitate remains at the side in the bottom and the siphon may be inserted to the bottom of the flask without contacting any precipitate. After siphoning off the original clear liquid, five successive 25-cc. charges (measured sufficiently accurately with a graduate) of 3 per cent sulfuric acid of carefully predetermined density, are introduced with intervening siphonings. After the introduction of each charge of acid, the flask contents are gently agitated by rotating the flask, conveniently while it floats inclined in a beaker partly filled with water. Violent shaking is to be avoided, as it breaks up the precipitate particles, causing a slight amount of the precipitate to float on the liquid surface as scum. After siphoning away as much as possible of the fifth charge of acid, 75 cc. of the 3 per cent acid are added and agitated with the precipitate. After the precipitate has settled, a pycnometer filled with the 3 per cent sulfuric acid is attached to the flask neck, as explained elsewhere (3), and the assembled apparatus is slowly inverted so that the precipitate of lead sulfate slides smoothly into the pycnometer. By giving the inverted apparatus a rotary motion a number of times, the precipitate is transferred to the pycnometer so completely that no centrifuging is required. If suitable centrifuge is available a more rapid transfer is accomplished by centrifuging a minute or two at about 1200 r. p. m. At this relatively low speed danger of leakage is so slight, if the pycnometer is tightly attached to the precipitation flask, that the centrifuge cup need not be filled with water during centrifuging.

When the transfer of the precipitate to the pycnometer is complete, the pycnometer is removed, its top is inserted firmly, and it is placed in a water bath at 30° C. After 15 minutes in the bath the height of the liquid in the pycnometer capillary is carefully adjusted to the scratch, by inserting through the capillary extremely narrow and slender slivers cut from filter paper. Then the pycnometer is withdrawn, the stopper and outer ground glass surface are carefully wiped dry with filter paper, and the dry ground glass cap is firmly put in place. The vessel may now be completely wiped dry, or preferably wiped over its outer surfaces with a moist cloth or chamois, then weighed after 15 to 20 minutes. The calculations of the results of the analyses are extremely simple (3).

## Results

The results of a series of pycnometric analyses for lead on two Bureau of Standards nonferrous alloys are given in Table I. The phosphor-bronze bearing metal, Standard Sample 63, contains nearly 10 per cent each of tin and lead, and about 78 per cent of copper. The lead-base bearing metal, Standard Sample 53, contains nearly 79 per cent of lead and about 10 per cent each of tin and antimony. Thus a copper-rich alloy and a lead-rich alloy have been subjected to pycnometric analysis. In both cases, by following the procedure outlined, using a 3 per cent sulfuric acid standard washing

liquid and an apparent density for lead sulfate of 5.791, analyses for lead are obtained in close agreement with Bureau of Standards averages. However, in the last analysis the density of the sulfuric acid liquor in which the precipitate formed was separately determined to be 1.2086, and the real density of 6.301 for lead sulfate was used in calculating the result.

TABLE II. PYCNOMETRIC ANALYSES FOR LEAD AS SULFATE

Sample	Weight Grams	Lead Found %	Lead Present %	Relative Error %
Alloy 63	1.0004	9.74	9.74	0.00
	2.0001	9.74		0.00
	2.00065	9.75		+0.10
	1.50095	9.75		+0.10
	1.0004	9.74		0.00
Alloy 53	0.19970	78.92	78.87	+0.06
	0.20020 <sup>a</sup>	78.84		-0.03
	0.99960	78.90		+0.04
	0.10035	78.74		-0.16
	0.51260 <sup>a</sup>	78.85		-0.03
	0.50750 <sup>a</sup>	78.88		+0.01
	0.21135 <sup>a,b</sup>	78.71		-0.20

<sup>a</sup> Analysis was made without use of centrifuge.

<sup>b</sup> Precipitate was not washed but density of supernatant liquid was separately determined.

## Discussion

The pycnometric method is readily adapted to the determination of lead as sulfate in nonferrous alloys. Employing 3 per cent sulfuric acid as standard washing medium, an apparent density considerably lower than the real density of the precipitate must be used, but the compensation for solubility losses of the precipitate thereby afforded, allows pycnometric results to be quickly and directly obtained in close agreement with gravimetric values obtained only after carrying out extra procedures for the recovery of small amounts of dissolved lead sulfate.

Because of the dependence of the apparent density of lead sulfate upon the strength and amount of sulfuric acid washing medium, as well as upon the general mode of the analysis, it is recommended that, having adopted a given analytical procedure, pycnometric analyses be carried out on samples of known lead content, and the proper value for the apparent density experimentally ascertained. This is readily done (3). The precision with which this precipitate density value needs to be known for calculating pycnometric analyses is diminished somewhat by the fortuitous fact that such calculations depend less strongly upon the value of the precipitate density in the case of denser precipitates (3). Thus in the case of the pycnometric method for lead any error in the value of the apparent density of lead sulfate appears in the calculated analyses diminished to about one fifth its original value and as an error of opposite sign.

A considerable simplification of the pycnometric method is offered in the case of lead sulfate because it is possible to dispense with the centrifuge. This should also be possible with other dense, compact precipitates which settle readily. There is also always the possibility of entirely omitting the washing of the precipitate and substituting for this operation a determination of the density of the liquid present along with the precipitate in the pycnometer.

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# Determination of Color and Turbidity in Solutions of Granulated Sugar

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A method has been devised for the determination of both color and turbidity in the same solution without filtration or other treatment. A photoelectric colorimeter is used and the readings are made using blue and yellow color filters. The apparatus is standardized by determining the relative percentage absorption of blue and yellow light by a given unit of color and turbidity. Knowing this relationship, it becomes a matter of simple calculation to express both color and turbidity as percentage of absorption of blue light, which in turn may be expressed in terms of the  $-\log$  of the transmission if desired.

The method is rapid and the results are reproducible. A colorimeter has not yet been devised which is suitable for routine control work.

SINCE the advent of photoelectric colorimeters of practical design, these instruments have been widely used in the sugar industry for the determination of color and turbidity of sugar solutions, sirups, etc. The results are obtained as percentage absorption or transmittancy of light through a column of solution of definite length. Since both color and turbidity influence the total light absorption, the value obtained is the sum of the two effects. In some cases the total percentage absorption (or transmittancy) is determined. The solution is then filtered to remove turbidity and the color is determined on the filtered solution. The turbidity is calculated by difference. This method has nothing to recommend it, because such filtration, if it removes practically all of the turbidity, invariably removes some of the color, so that the determined color is too low and the calculated turbidity is too high. Other instruments have been designed to determine total color and turbidity in the usual way and to determine turbidity alone by the Tyndall beam method, thus permitting a calculation of color to be made. Numerous references to various methods are found in the literature (1, 3, 4, 6, 7).

Recently Keane and Brice (5) have described a method for determining both color and turbidity in granulated sugar solutions without filtration, using an instrument of their own design. Two light filters are employed, Corning Glass Company light blue green No. 428 and signal red No. 245. Their method is based on two assumptions: that a given unit of turbidity gives approximately the same percentage absorption with either filter; and that the spectral characteristics of the red filter are such that the absorption is practically unaffected by the color of the solution and may be considered as due to turbidity alone. The turbidity is measured directly as the percentage absorption of red light. Color is calculated from the relationship of the transmittancies of

green and red light by an empirical formula and reported in terms of percentage absorption.

The writer, using a Lange colorimeter, has not been able to substantiate the assumption that the absorption of red light is unaffected by the color of the solution or that the effect of turbidity is the same when using both filters.

The figures tabulated in Table I are typical of numerous tests that were made to check the validity of this assumption. It is shown that the percentage absorption increases with increasing color, regardless of the type of color filter used. (The Lange red filter very closely resembles Corning signal red No. 245.) The turbidity, as calculated by the formula given below, is also included to show that the increased absorption shown by the red filters is not due to increasing turbidity. It is evident that readings obtained with the Lange colorimeter and calculated according to the method of Keane and Brice would give too high values for both turbidity and color.

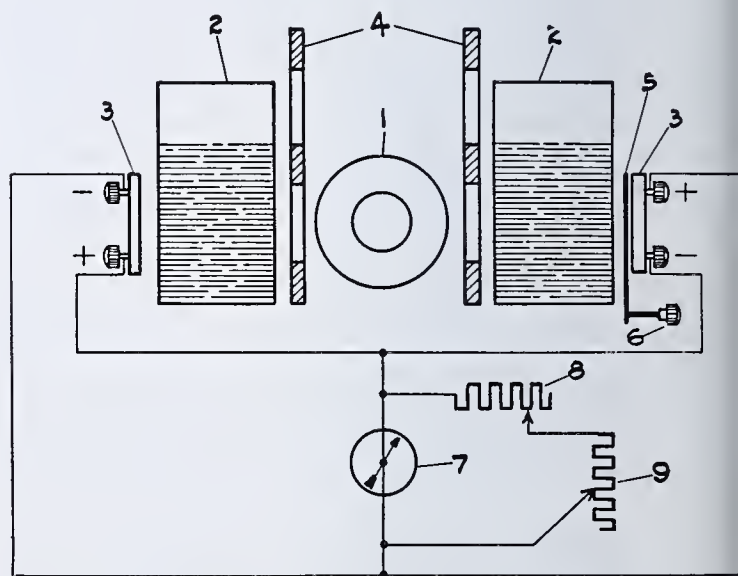


FIGURE 1. LANGE COLORIMETER

- |                        |                     |
|------------------------|---------------------|
| 1. Lamp                | 5, 6. Shutter plate |
| 2. Solution cells      | 7. Galvanometer     |
| 3. Photoelectric cells | 8, 9. Rheostats     |
| 4. Color filters       |                     |

The idea of determining color and turbidity on the same solution is very attractive and further investigation of the possibilities resulted in the development of the method described here.

## The Instrument

The Lange colorimeter is simple and compact. Its chief disadvantage is that the column of solution under examination is only 34 mm. in depth. Nevertheless, results in the range of 1.0 to 5.0 per cent absorption (the range covered by ordinary granulated sugar solutions) are reproducible to within  $\pm 0.2$  per cent. A higher degree of accuracy is desirable and can be had with instruments of equal sensitivity but designed to use a longer column of solution. A diagram of the instrument is shown in Figure 1. A series of color



TABLE I. EFFECT OF COLOR ON PERCENTAGE LIGHT ABSORPTION  
(Using various color filters)

Caramel Added to Filtered Sugar Solution Ml./100 ml.	Blue <sup>a</sup>	Blue- green <sup>b</sup>	Yel- low <sup>a</sup>	Orange- red <sup>c</sup>	Red <sup>a</sup>	Calcu- lated Turbid- ity
0.5	2.2	1.3	0.75	0.4	0.45	0.05
1.0	4.5	2.5	1.45	0.9	0.9	0.00
1.5	6.5	3.8	2.10	1.2	1.0	0.00
2.0	8.3	4.6	2.7	1.7	1.4	0.05

<sup>a</sup> Color filters supplied with Lange colorimeter.  
<sup>b</sup> Corning, light blue-green No. 428.  
<sup>c</sup> Corning, lighthouse red No. 246.

lters are supplied with it. After many trials the blue and yellow filters were selected as being most satisfactory. The spectral characteristics of the filters as given by the maker are shown in Figure 2. The blue filter was selected because it is very nearly complimentary to the color of the average sugar solution and consequently a relatively high percentage absorption is obtained for a given unit of color. The yellow filter gives a much lower percentage absorption for a given color intensity than the blue and the readings are more easily reproducible than those of the orange or red filters. The scale of the instrument contains 100 divisions and can be operated to read directly in percentage absorption. The balancing rheostats, however, may be adjusted so as to increase the sensitivity, in which case a deflection of one scale division is equivalent to a fraction of 1 per cent absorption. In this work the adjustment was made to maximum sensitivity and actual percentage absorption was obtained by dividing the net deflection by 2.3 when using the blue filter and 3.6 when using the yellow filter. These factors were determined by comparing the readings obtained at normal sensitivity with those obtained for the same solution at maximum sensitivity.

STANDARDIZATION OF THE INSTRUMENT. A clear, colorless sugar solution containing 50 grams of sugar per 100 ml. was first prepared. This was made from highest purity sugar, treated with Super-Norit or other high-grade carbon, then filtered through especially prepared Filter-Cel. This solution serves as the standard and is assumed to have zero absorption. (Distilled water cannot be used as a primary reference standard because it is as a lower transmissivity per unit depth than a sugar solution.) The glass solution cell which was to be used in future determinations was filled with this solution and another cell with distilled water and the difference in deflection of the instrument determined for both color filters, to give the "cell correction constant." This constant is made up of the difference in optical characteristics of the cells, as well as the difference between water and sugar solutions. Its application permits the use of water as reference standard when making routine measurements. The next step in the standardization was to determine the relative percentage absorption for a given unit of color when using the blue and yellow filters. This was done by adding to a sugar solution successive small quantities of caramel solution which had been filtered through Filter-Cel, and determining the percentage absorption for each color filter. This operation was repeated a number of times, starting with standard sugar solutions as described above and with solutions of ordinary granulated sugar. An average figure was computed and it was found that the ratio of absorption with blue light to that with yellow light was 2.85 to 1.00—that is, if an absorption of 2.85 per cent is obtained with the blue light, an absorption of 1.00 per cent will be obtained with yellow light. In the same way by varying the turbidity and having the color remain constant, a relative effect of turbidity on the two types of light was determined and found to be in the ratio of 1.05 to 1.00 for the blue and yellow, respectively. This relation was established by using solutions of ordinary granulated sugar and comparing the percentage absorption of blue and yellow light before and after filtration through paper in the manner described below. The factor was arrived at by averaging some 200 determinations. The data under "Total Percentage Absorption" in Table II will serve to illustrate the method. It is evident that no significant error would be introduced if one assumed the factor to be 1.0 instead of 1.05. Having determined these ratios for the relative

effect of color and turbidity, it is a matter of simple calculation to determine the proportion of the total percentage absorption of any test solution which is due to color and turbidity.

Let  $a$  = total percentage absorption with the blue filter  
 $b$  = total percentage absorption with the yellow filter  
 $x$  = percentage absorption of blue light due to color  
 $y$  = percentage absorption of blue light due to turbidity

Then  $x + y = a$  (1)

$$\frac{x}{2.85} + \frac{y}{1.05} = b$$

or  $1.05x + 2.85y = 2.95b$  (2)

Solving for  $x$  and  $y$

$$y = \frac{2.85b - a}{1.70} = \text{percentage absorption due to turbidity} \quad (3)$$

$$x = a - y = \text{percentage absorption due to color} \quad (4)$$

Both color and turbidity are thus expressed in terms of percentage absorption of blue light.

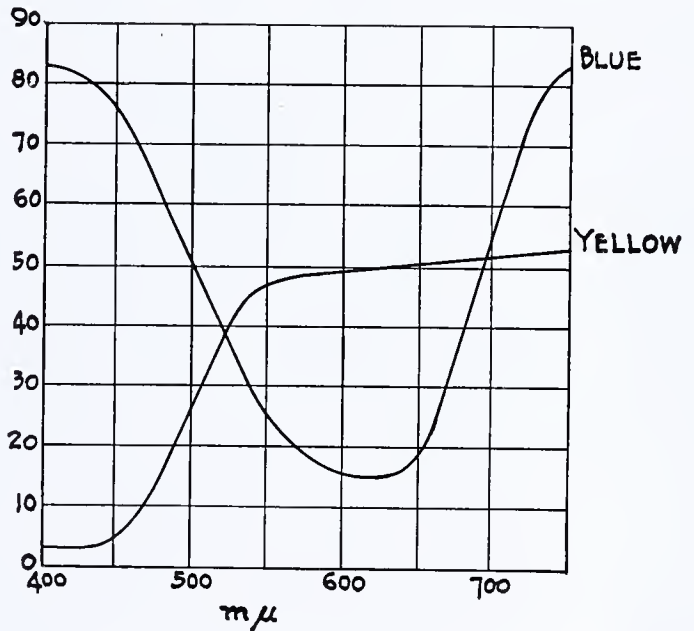


FIGURE 2. TRANSMISSION OF COLOR FILTERS

It is evident that the relation between the blue and yellow absorption will vary with change in the spectral character of the color to be measured. The color in refined cane sugars is probably nearly all due to caramel or the decomposition products of invert sugar, while in beet sugars the color is only slightly influenced by the presence of these substances. Therefore to make the method applicable to beet sugars, it became necessary to determine the blue-yellow absorption ratio for the type of color found in them. This was done by using high raw sugars as the source of color. The solutions were filtered with Filter-Cel to remove, as nearly as possible, all turbidity. Portions of these solutions were mixed with granulated sugar solution which had likewise been treated for the removal of turbidity. The ratio between the blue and yellow absorption as determined by this method was 3.1 to 1.0.

The equation becomes

$$y = \frac{3.07b - a}{1.95}$$

or simply  $y = \frac{3.1b - a}{2.0} = \text{turbidity}$

### Description of Method

Test solutions are made up containing 50 grams of sugar per 100 ml., brought to the boiling point to expel the air, then cooled to room temperature. (Solutions containing invert sugar should be de-aired without heating.) The net deflection is obtained for both color filters by comparison with



TABLE II. PERCENTAGE ABSORPTION

Sample	Total Percentage Absorption				Percentage Absorption Due to Color		Calculated Values Percentage Absorption Due to Turbidity	
	Unfiltered	Yellow	Blue	Filtered	Unfiltered	Filtered	Unfiltered	Filtered
1	2.18	1.33	1.74	0.82	1.21	1.34	0.97	0.40
2	2.70	1.62	2.18	1.14	1.54	1.50	1.16	0.68
3	2.59	1.33	2.28	1.14	1.82	1.65	0.77	0.63
4	3.26	1.89	2.61	1.33	1.96	1.85	1.30	0.76
5	1.74	0.82	1.61	0.78	1.34	1.21	0.40	0.40
6	3.48	2.19	2.61	1.36	1.83	1.80	1.65	0.81
7	4.35	2.72	3.83	2.17	2.31	2.38	2.04	1.45
8	4.45	3.25	3.13	1.92	1.62	1.72	2.83	1.41
9	2.52	1.33	2.17	1.05	1.72	1.63	0.80	0.54
10	2.17	1.25	1.87	0.90	1.31	1.34	0.86	0.53
11	2.35	1.31	1.96	1.03	1.50	1.34	0.85	0.62
12	1.83	1.01	1.70	0.78	1.18	1.34	0.65	0.36
13	2.87	1.56	2.52	1.19	1.88	1.88	0.99	0.64
14	2.63	1.47	2.17	1.05	1.66	1.63	0.97	0.54
15	2.52	1.29	2.24	1.05	1.78	1.73	0.74	0.51
16	2.09	1.05	1.74	0.78	1.50	1.40	0.59	0.34
17	3.09	2.06	2.39	1.31	1.45	1.55	1.65	0.84
18	3.14	1.64	2.83	1.33	2.17	2.18	0.97	0.65
19	2.52	1.17	2.35	1.03	1.96	1.92	0.56	0.43
20	3.52	2.08	2.92	1.53	2.05	2.00	1.47	0.92

TABLE III. COLOR AND TURBIDITY TESTS

	Original	Caramel Added					
		1.0 ml.	2 ml.	3 ml.	4 ml.	5 ml.	6 ml.
Sugar No. 1, Unfiltered Solution							
Color	1.6	2.4	3.2	4.0	4.4	5.1	5.5
Turbidity	1.3	1.3	1.1	1.1	1.3	1.5	1.5
Sugar No. 1, Filtered through Paper							
Color	1.7	2.1	3.3	3.7	4.7	5.2	5.6
Turbidity	0.8	0.9	0.7	0.8	0.7	0.9	0.9
Sugar No. 1, Filtered through Filter-Cel							
Color	1.3	2.1	3.0	3.6	4.1	5.1	5.7
Turbidity	0.4	0.3	0.4	0.5	0.6	0.6	0.6
Sugar No. 2, Unfiltered Solution							
Color	1.2	2.3	3.1	3.5	4.0	4.9	5.4
Turbidity	2.8	2.6	2.5	2.5	2.5	2.4	2.4
Sugar No. 2, Filtered through Paper							
Color	1.3	2.3	2.6	3.5	3.8	4.7	5.2
Turbidity	1.3	1.1	1.5	1.3	1.4	1.3	1.3
Sugar No. 2, Filtered through Filter-Cel							
Color	0.7	1.5	2.3	2.9	3.7	4.3	5.1
Turbidity	0.3	0.4	0.3	0.3	0.3	0.2	0.2
Sugar No. 3, Unfiltered Solution							
Color	1.4	1.8	3.0	3.8	4.0	5.0	5.5
Turbidity	1.3	1.4	1.2	1.2	1.4	1.3	1.3
Sugar No. 4, Unfiltered							
Color	1.5	2.0	3.0	3.3	4.0	4.7	5.4
Turbidity	2.9	3.0	3.0	3.0	3.0	2.9	2.8
Sugar No. 5, Unfiltered							
Color	1.6	2.3	3.1	3.3	4.3	5.0	5.5
Turbidity	1.5	1.4	1.5	1.7	1.4	1.4	1.5

water and applying the cell correction described above. The percentage absorption is calculated by dividing the net deflection by 2.3 for the blue filter and 3.6 for the yellow filter. The color and turbidity are then calculated according to the formula.

Discussion of Results

This method of color and turbidity analysis has been applied to several hundred samples of granulated sugar. In most cases determinations were made on the original solution and on the same solution after double filtration through filter paper (B & A, Grade A) on a Büchner funnel. This sort of filtration removes coarse suspended matter, but not color or colloidal matter.

The total percentage absorption for both color filters, for filtered and unfiltered solutions, as well as the calculated values for color and turbidity, are given in Table II for twenty different sugars. The results tabulated here were selected to represent the various types of sugar ordinarily encountered. For example, Nos. 1, 5, and 12 are low in both color and turbidity; No. 7 is high in both color and turbidity; No. 8,

which shows a high total absorption, is relatively low in color and high in turbidity; and No. 18 is high in color and low in turbidity. There is a wide variation in the amount of turbidity removed by filtration. This merely means that a variable percentage of the total turbidity is made up of suspended particles which are filterable on paper. The color of the filtered and unfiltered solutions agrees within the limits of error of the method (about  $\pm 0.2$  per cent) regardless of the variation in turbidity. It is, therefore, possible to measure variations in turbidity while the color remains constant.

Tests were also made in which the color varied while the turbidity remained constant. This was done by adding successive portions of caramel to sugar solutions, and calculating the color and turbidity for each increment of color. The details of the tests and the results are shown in Table III. It will be noted that the turbidity remains practically constant throughout any given series. There are occasional discrepancies in both color and turbidity which are probably due to errors in reading the instrument.

The method has been tested under two sets of conditions: constant color and variable turbidity, and constant turbidity and variable color. It has been found adequate in defining both conditions.

The method as herein described is empirical in that the results are expressed in terms of percentage absorption of a particular blue light by a column of solution 34 mm. deep, the light source being a 25-watt tungsten-filament lamp at 110 volts. It is applicable for measuring color intensity and turbidity in solutions in which the spectral characteristics of the color remain practically constant, and where the total absorption does not exceed 8 to 10 per cent. Beyond this point the deviation from the assumed direct proportionality between the percentage absorption and the concentration of light-absorbing substances exceeds the limits of error of the method. It is possible, however, to extend the application to juices, sirups, and other solutions of high percentage absorption by substituting the value of  $-\log T$ , where  $T$  is the percentage transmission, for the percentage absorption in the equation. If the measurements are carried out at constant concentration of sugar and at constant depth of solution,  $-\log T$  is proportional to the concentration of light-absorbing substances. By the application of Lambert and Beer's law the results may be reduced to terms of unit concentration and unit depth. For details of the theoretical considerations involved the reader is referred to Eggert and Gregg (2).

The principles of the method can also be applied to colorimetric analysis where turbidity is an interfering factor, or for the determination of precipitates in terms of turbidity in



colored solutions. Any suitable pair of color filters may be used. In any case the absorption ratios of the filters must be determined for the color and turbidity in question and these ratios must remain approximately constant for the range of conditions under investigation.

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# Selective Oxidation of Levulose with Potassium Ferricyanide

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THE alkaline copper sulfate solution of Fehling (3) was probably the first chemical reagent used for the determination of sugars and even today the copper methods still outnumber all others. In 1859, however, Gentele (4) made use of an alkaline potassium ferricyanide solution for the determination of reducing sugars in the presence of sucrose and dextrans. Apparently not much work was done with this reagent until the advent of the Hagedorn-Jensen method (5) for blood sugar. Since that time its scope has been widened until today it is a very valuable reagent for the biochemist and is becoming increasingly more so for the sugar analyst. Since 1929 Hanes (6), Callow (1), Hulme and Narin (8), Cole (2), Miller and Van Slyke (12), and several others have modified and expanded the Hagedorn-Jensen method to include other sugars of biochemical interest, while Whitmoyer (18), Hassid (7), and Strepkov (15) have utilized it for the analysis of plant extracts and sugar solutions. Its reported freedom from atmospheric oxidation, lack of filtration necessity, and the ease and accuracy with which its reduced form can be determined are factors which recommend it very highly.

Within the last two years, another property of this reagent has been discovered—its ability to oxidize levulose selectively in the presence of dextrose. Strepkov (14) has developed a micromethod for this determination using an alkaline ferricyanide solution as the oxidizing agent. Two cubic centimeters of the alkaline potassium ferricyanide reagent [1.65 grams of potassium ferricyanide and 80 grams of sodium monohydrogen phosphate dodecahydrate per liter] and 1 cc. of sugar solution containing up to 1.5 mg. of levulose are heated in a closed tube at 60° C. for 2.5 hours. After this time the solution is cooled, and acidified with 10 per cent acetic acid, 2 cc. of an iodine solution are added, and the excess is titrated with 0.005 *N* thiosulfate. Dextrose in amounts up to 0.5 mg. is reported to have no reducing action. In the experimental work reported below it is shown, however, that dextrose does have a definite reducing action, but only a small fraction of that of levulose, and an attempt was made to find conditions which would decrease its action even more. One of the conditions studied was that caused by the addition of phosphate.

It has been known for many years that phosphate has a definite effect upon the oxidation of sugars, but the question as to what the effect is remains a point of controversy. Kappanna (9) reports that the iodometric oxidation of dextrose to gluconic acid in a solution buffered to pH 7 with

phosphate does not occur at all, and that at a constant alkalinity the phosphate concentration has no effect. Theriault, Butterfield, and McNamee (16), working with pH values in the physiological range and temperatures of 20° to 50° C., found that the oxidation of dextrose by atmospheric oxygen was not catalyzed by phosphates. According to Malkov and Zwetkova (11) the oxidation of dextrose by hydrogen peroxide in the presence of ferrous sulfate is inhibited by phosphate, while in the absence of hydrogen peroxide a catalytic action is observed. Work by Kuen (10) shows that at a pH of 7 the oxidation of dextrose by hydrogen peroxide is increased fourfold in the presence of phosphate, and Witze-mann (19) states that sodium hydrogen phosphate is a specific catalyst for this reaction. Warburg and Yabusoe (17) and Nicloux and Nebenzahl (13) found that phosphate catalyzes the oxidation of levulose. In this paper, experimental results indicate that under the conditions used the rate of oxidation of levulose by potassium ferricyanide in alkaline solution is affected very little by phosphate, while the oxidation of dextrose is inhibited.

The catalytic action of traces of iron is well known and undoubtedly the ferricyanide reagent furnishes enough ferric ions to bring this factor into operation.

### Experimental

The levulose used in these experiments was a pure-white crystalline product with a specific rotation of  $-91$  and the dextrose was a crystalline product with a specific rotation of  $+52.5$ ; the inorganic reagents were of analytical grade. During all the determinations, the constant-temperature water bath was maintained within  $\pm 0.1^\circ$  C. of the specified temperature. The concentration of both the dextrose and the levulose solutions was 1 mg. per cc. and 10-cc. portions were used for each analysis.

Throughout all the work the following procedure was used for each analysis. A 10-cc. portion of the sugar solution was placed in a 125-cc. Erlenmeyer flask and 25 cc. of the alkaline potassium ferricyanide reagent were added from a graduated cylinder. A strip of sheet lead made into a collar and fitted over the neck of the flask prevented its tipping or floating when placed in water deep enough to cover it several centimeters above the level of the solution inside. As soon as the solution reached the water-bath temperature, the flasks were stoppered to prevent any oxidation of potassium ferrocyanide by atmospheric oxygen. Tests were carried out by heating a standard ferrocyanide solution in both stoppered and unstoppered flasks for 2 hours at 50° C. At the end of this period of heating both showed a slight oxidation, but the unstoppered flask about 1.2 per cent more than the stoppered.

At specific intervals of time the flasks were removed from the water bath, cooled under a tap, and acidified with 6 *N* sulfuric



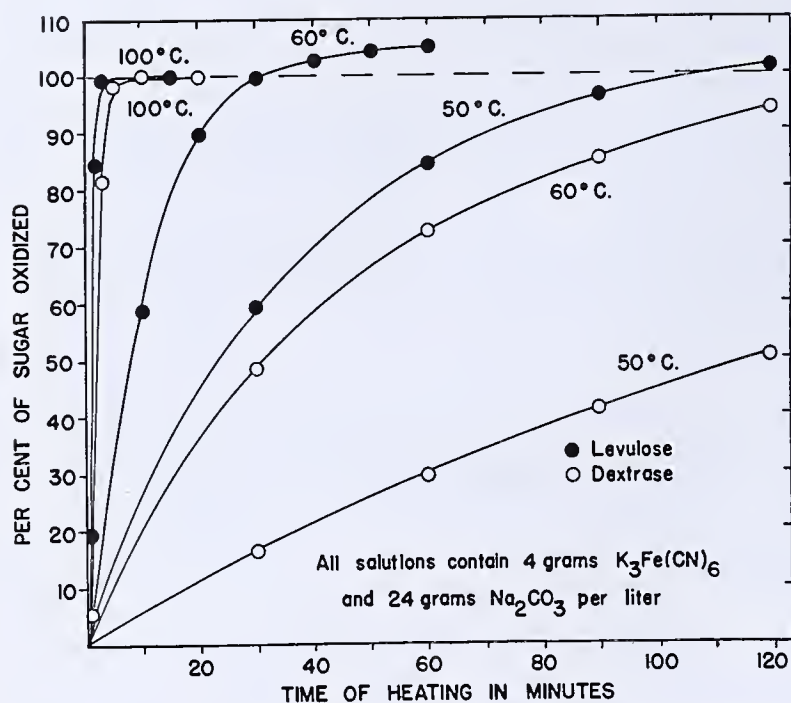


FIGURE 1. EFFECT OF TEMPERATURE ON RATES OF OXIDATION WITH SODIUM CARBONATE BUFFER

TABLE I. SUGAR OXIDIZED AT 50° AND 60° C.

(Solution containing 24 grams of  $\text{Na}_2\text{CO}_3$  and 40 grams of  $\text{K}_3\text{Fe}(\text{CN})_6$  per liter)

Time of Heating Min.	At 50° C.		At 60° C.	
	Dextrose %	Levulose %	Dextrose %	Levulose %
10	..	22.9	..	58.7
20	..	44.9	..	89.9
30	16.8	59.6	48.9	99.3
40	..	72.0	..	102.7
50	..	82.1	..	104.2
60	29.9	84.5	72.8	105.0
70	..	88.9	..	..
80	..	92.5	..	..
90	41.5	96.2	85.1	..
100	..	98.4	..	..
110	..	99.8	..	..
120	50.8	101.6	94.0	..

acid; special care was taken to avoid spattering, particularly when the concentrated carbonate solutions were used. Two drops of a 0.025 *M* solution of *o*-phenanthroline-ferrous sulfate indicator solution were added and titrated to the disappearance of the orange color with a standard ceric sulfate solution about 0.02 *N*. An indicator blank correction of 0.15 cc. was subtracted from all titration values.

**TIME-TEMPERATURE EFFECT.** Pure dextrose and levulose solutions were heated in the water bath at 50° and 60° C., and on the steam cone for varying lengths of time with 25 cc. of the alkaline potassium ferricyanide reagent used by Hassid (4.0 grams of potassium ferricyanide and 24 grams of sodium carbonate per liter). Table I and the second column of Table II indicate that the oxidation rate of both sugars was

TABLE II. SUGAR OXIDIZED BY BOILING

(Solutions containing  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ )

Time of Heating Min.	12 Grams $\text{Na}_2\text{CO}_3$ per Liter		24 Grams $\text{Na}_2\text{CO}_3$ per Liter		80 Grams $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ per Liter	
	Dextrose %	Levulose %	Dextrose %	Levulose %	Dextrose %	Levulose %
1	..	15.6	5.6	19.0	0.0	0.4
2	34.0	72.5	..	84.2	0.6	6.8
3	69.7	95.6	81.4	99.2	3.8	20.8
4	83.3	97.0	..	99.7	7.3	25.0
5	94.8	99.5	98.1	99.8	10.0	27.1
6	96.9	99.5	99.4	..	12.6	43.8
7	98.2	100.0	99.5	99.9	15.6	50.6
8	99.6	99.6	99.7	..	14.4	58.3
9	100.1	99.8	99.9	..	20.8	64.1
10	100.0	100.0	100.0	100.0	22.6	69.0
15	100.3	100.1	100.0	100.0	27.9	79.6
20	..	..	99.6	100.0	35.2	88.4
25	..	..	..	..	39.4	101.0
30	..	..	..	..	50.2	105.4

greatly increased at higher temperatures, but in each case the levulose was oxidized more rapidly than the dextrose. At 50° C. there is a distinct difference in the rate of oxidation of the two sugars, but this difference decreases with increasing temperature until, as Figure 1 shows, the rates are almost the same at 100° C.

In all the tables, the results are expressed as per cent of sugar oxidized. The 100 per cent value was arbitrarily accepted as the figure obtained on heating the sugar solution for 10 minutes on a steam cone with the alkaline ferricyanide reagent of the composition described by Hassid. This choice was justified to some extent since, as can be seen from Table II, the titration value reaches a maximum within 10 minutes and remains constant upon heating for an additional 10 minutes. When lower temperatures and longer times were used, the oxidation often reached a value in excess of this figure, probably as a result of some secondary oxidation reaction.

**EFFECT OF CARBONATE CONCENTRATION.** The sodium carbonate concentration of the alkaline ferricyanide reagent was changed from 24 to 12 and 48 grams per liter while the temperature was held at 50° C. The data in Tables I and III show that the effect was to increase the oxidation rate of both sugars with an increase in the carbonate concentration. An almost linear proportionality seems to exist between the reaction rate and the carbonate concentration, as

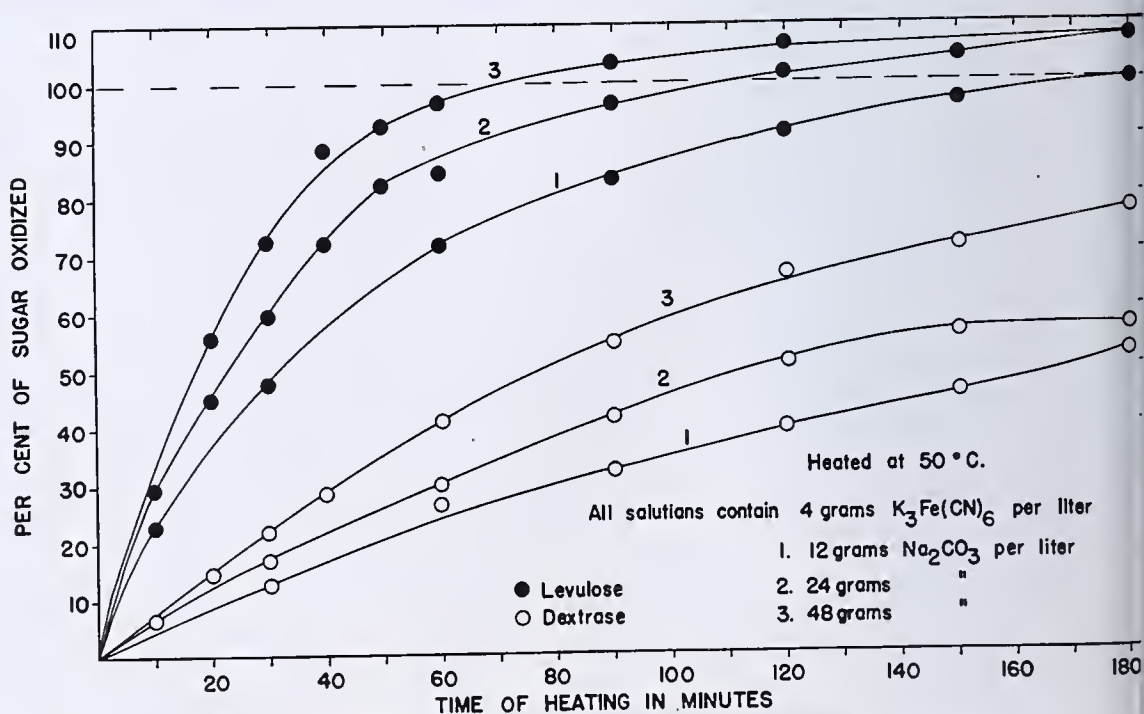


FIGURE 2. EFFECT OF CARBONATE CONCENTRATION ON RATES OF OXIDATION AT 50° C.



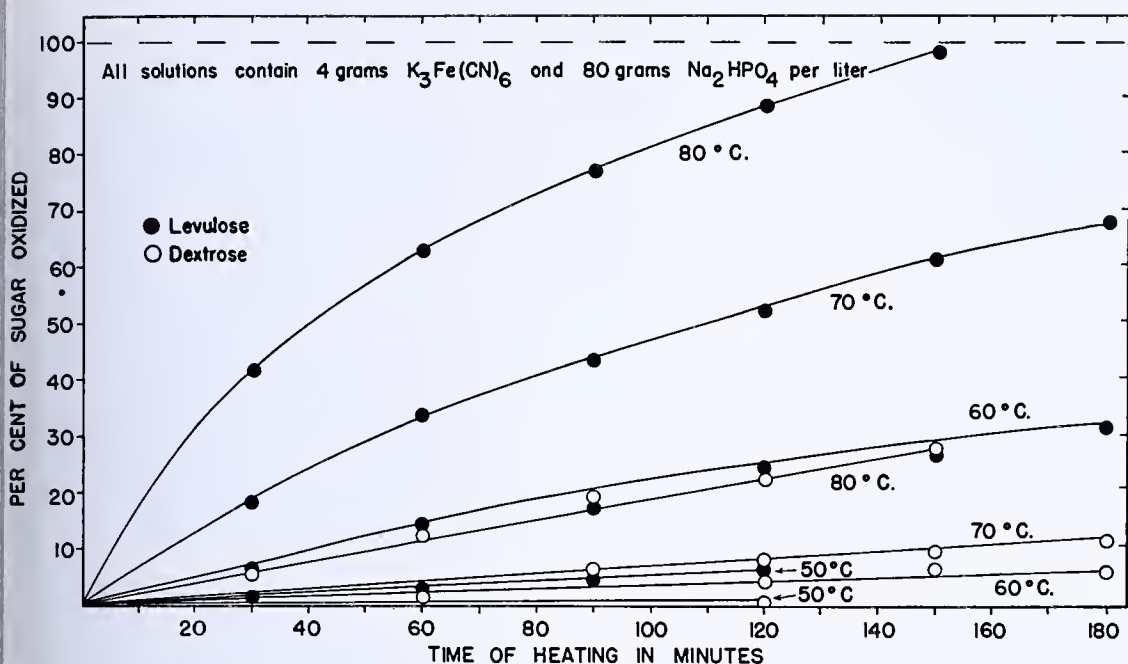


FIGURE 3. EFFECT OF TEMPERATURE ON RATES OF OXIDATION WITH PHOSPHATE BUFFER

shown in Figure 2. Increasing the ferricyanide concentration from 4.0 to 8.0 grams per liter produced no change in the reaction.

**EFFECT OF PHOSPHATE.** In an attempt to duplicate the results obtained by Strepkov (14), the recommended phosphate-ferricyanide solution containing 1.5 grams of potassium ferricyanide and 80 grams of sodium hydrogen phosphate per liter was used at 60° C. In no case was there even an approach to the results reported by him. In every instance the dextrose was 15 per cent or more oxidized by the time the levulose was completely oxidized. It is true, of course, that the conditions under which the experiments were carried out were not exactly the same. In one case a micro scale (0.1 to 1.5 mg. of sugar) was used and the ferrocyanide determined iodometrically, while in the other a semimicro scale (10 mg. of sugar) was used and the ferrocyanide determined by ceric sulfate titration. Nevertheless, it is rather difficult to see how these differences in technique could cause such a variation in the results obtained.

When it became apparent that these conditions did not lead to a satisfactory selectivity in oxidation, the temperature and ferricyanide concentration were changed. Temperatures of 50°, 60°, 70°, and 80° C. and boiling were tried and ferricyanide concentrations of 1.5 and 4.0 grams per liter were used. In all these experiments the sodium hydrogen phosphate concentration was 80 grams per liter. These results are given in Table IV.

With this phosphate buffer, a marked decrease was noted in the oxidation rate of both sugars, but the dextrose oxidation was inhibited much more than the levulose, so that the result was a greater spread between the curves for the two

sugars (Figure 3). Even at 80° C., almost 160 minutes were required for the complete oxidation of levulose and at lower temperatures a proportionally longer time was necessary.

**EFFECT OF PHOSPHATE AND CARBONATE.** An effort was made to utilize the differential oxidation promoted by the phosphate and the increased rate of reaction caused by the carbonate by combining varying proportions of the two with the potassium ferricyanide. An alkaline ferricyanide solution composed of 4.0 grams of potassium ferricyanide, 10 grams of sodium carbonate, and 80 grams of sodium hydrogen phosphate per liter was tried at tem-

peratures of 50°, 55°, 60°, and 70° C. Table V shows the same general relationship between reaction rate and temperature as in the case of the carbonate and phosphate buffers when used separately.

TABLE III. SUGAR OXIDIZED AT 50° C.

(With various Na<sub>2</sub>CO<sub>3</sub> concentrations)

Time of Heating Min.	12 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter		48 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter	
	Dextrose %	Levulose %	Dextrose %	Levulose %
10	..	...	6.5	29.0
20	..	...	14.4	55.5
30	12.4	47.5	21.9	72.2
40	..	...	28.5	88.5
50	..	...	...	92.5
60	26.4	71.9	41.0	96.8
90	32.0	83.0	54.5	103.3
120	39.6	91.0	66.1	106.9
150	45.5	96.7	71.1	103.2
180	52.4	100.0	77.2	107.4

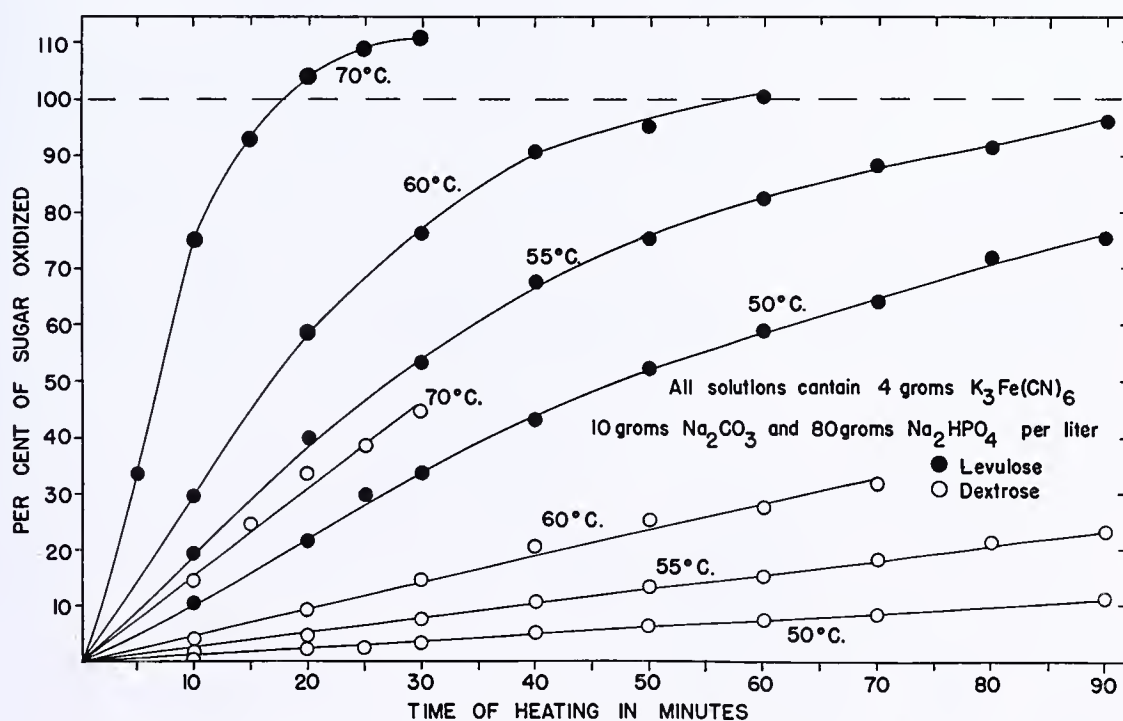


FIGURE 4. EFFECT OF TEMPERATURE ON RATES OF OXIDATION WITH CARBONATE-PHOSPHATE BUFFER



TABLE IV. SUGAR OXIDIZED AT VARIOUS TEMPERATURES WITH A  $\text{Na}_2\text{HPO}_4$  BUFFER

Time of Heating Min.	At 50° C.		At 60° C.		At 70° C.		At 80° C.	
	Dextrose %	Levulose %	Dextrose %	Levulose %	Dextrose %	Levulose %	Dextrose %	Levulose %
30	0.0	1.6	...	6.5	..	18.0	5.7	41.6
60	0.0	2.9	1.3	14.7	..	33.6	12.6	62.9
90	0.0	4.6	...	17.0	6.2	43.4	19.4	77.0
120	0.3	6.2	4.5	24.5	8.0	52.3	22.3	88.5
150	...	...	6.5	26.9	9.8	61.5	28.0	98.2
180	...	...	5.8	31.8	11.4	67.8	..	..

TABLE V. SUGAR OXIDIZED BY HEATING

(Mixed phosphate-carbonate buffer, 80 grams of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and 10 grams of  $\text{Na}_2\text{CO}_3$  per liter, at various temperatures)

Time of Heating Min.	At 50° C.		At 55° C.		At 60° C.		At 70° C.	
	Dextrose %	Levulose %	Dextrose %	Levulose %	Dextrose %	Levulose %	Dextrose %	Levulose %
5	..	..	..	..	..	..	4.9	33.6
10	0.7	10.5	1.9	19.2	4.1	29.5	14.9	75.5
15	..	..	..	..	..	..	24.9	93.1
20	2.2	21.8	4.9	39.9	9.1	58.7	33.6	104.3
25	2.8	29.9	..	..	..	..	38.3	109.1
30	3.7	33.7	7.6	53.1	14.9	76.7	44.7	111.2
40	5.3	43.4	10.6	67.6	20.4	91.0	..	..
50	6.6	52.1	13.1	75.4	25.3	95.8	..	..
60	7.9	59.1	15.4	82.7	27.9	100.8	..	..
70	..	64.1	18.7	88.5	32.2	..	..	..
75	9.4	..	..	..	..	..	..	..
80	..	72.0	21.5	91.6	..	..	..	..
90	11.3	75.4	23.4	95.7	..	..	..	..

The 50° C. temperature was most satisfactory for two reasons: (1) because, as can be seen from Figure 4, the rate of oxidation for dextrose is much slower than at higher temperatures; (2) because this temperature is much easier to attain and maintain accurately than a higher one. The 50° C. temperature was therefore chosen as standard and used in all the following experiments.

With the phosphate concentration remaining at 80 grams per liter, the sodium carbonate concentration was varied from 10 through 70 grams per liter in steps of 10. The result, as given in Table VI, was a progressive decrease in the time of oxidation up to 50 grams per liter and then practically no change

through 70 grams per liter. The net result was an improvement of about 3 per cent in the spread of the oxidation rates of the two sugars and a decrease of about 45 minutes in the time required for the levulose to react completely. For greater ease of comparison, some of these results are presented graphically in Figure 5.

These results led to the investigation of still higher carbonate concentrations with accompanying increases in the phosphate concentration in an effort to decrease the dextrose oxidation without decreasing the rate of levulose oxidation. Solutions containing 4.0 grams of potassium ferricyanide per liter and the following phosphate and carbonate concentrations were made up:

	$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ G./l.	$\text{Na}_2\text{CO}_3$ G./l.
1	160	70
2	80	160
3	200	200
4	160	160
5	250	150

As the figures in Table VII show, solution 5 caused the complete oxidation of

TABLE VI. SUGAR OXIDIZED AT 50° C.

(With 80 grams of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  per liter and with various  $\text{Na}_2\text{CO}_3$  concentrations)

Time of Heating Min.	20 Grams $\text{Na}_2\text{CO}_3$ per Liter		30 Grams $\text{Na}_2\text{CO}_3$ per Liter		40 Grams $\text{Na}_2\text{CO}_3$ per Liter		50 Grams $\text{Na}_2\text{CO}_3$ per Liter		60 Grams $\text{Na}_2\text{CO}_3$ per Liter		70 Grams $\text{Na}_2\text{CO}_3$ per Liter	
	Dex- trose %	Levu- lose %	Dex- trose %	Levu- lose %	Dex- trose %	Levu- lose %	Dex- trose %	Levu- lose %	Dex- trose %	Levu- lose %	Dex- trose %	Levu- lose %
15	..	..	..	..	..	..	5.8	42.0	3.7	45.0	3.6	42.7
20	..	..	3.4	38.5	5.8	44.5	..	..	..	..	..	..
25	3.5	40.9	..	..	..	..	8.1	69.9	7.6	73.1	8.2	72.3
30	..	..	..	..	..	..	..	..	..	..	..	..
40	..	..	8.2	67.0	8.8	73.5	..	..	..	..	..	..
45	..	..	..	..	..	..	12.2	89.0	11.6	87.5	11.9	89.4
50	9.4	71.9	..	..	..	..	..	..	..	..	..	..
60	..	..	12.2	84.3	14.0	92.1	18.5	101.5	15.3	97.4	15.0	95.8
75	13.6	88.0	..	..	..	..	19.4	108.3	19.2	104.0	19.1	103.9
80	..	..	15.5	95.2	18.8	103.8	..	..	..	..	..	..
100	19.0	98.7	19.0	101.8	20.4	106.0	..	..	..	..	..	..
125	22.9	101.5	..	..	..	..	..	..	..	..	..	..

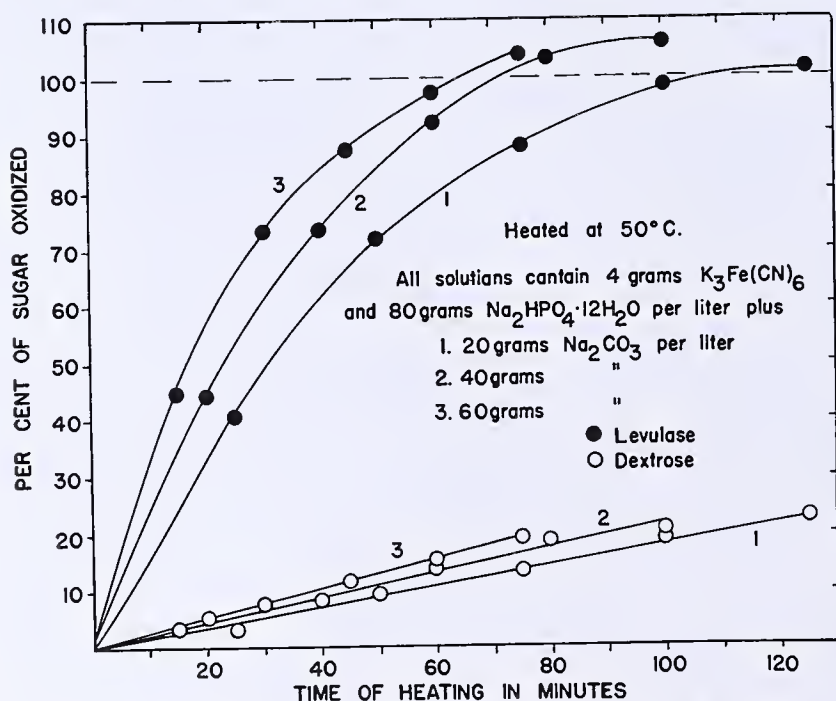


FIGURE 5. EFFECT OF CARBONATE CONCENTRATION ON RATES OF OXIDATION AT 50° C. WITH CARBONATE-PHOSPHATE BUFFER

levulose at 50° C. in less than 40 minutes and gave the greatest differential in the rate of reaction. Some typical results are given graphically in Figure 6.

### Discussion of Results

Using only sodium carbonate as the alkalinizing agent produced no satisfactory differential oxidation of the sugars. An increase in the carbonate concentration produced a marked increase in the rate of reaction of both sugars but was not at all selective in its action. The increase was probably due to an increase in pH and not to any specific property of the sodium carbonate. The temperature effect was essentially the same as that of the carbonate but even more pronounced. A 10° C. rise in temperature (from 50° to 60° C.) shortened the time of complete oxidation of levulose by 73 per cent, while doubling the carbonate concentration caused only a 38 per cent reduction in time.

With sodium hydrogen phosphate as the alkaline buffer, the oxidation is much slower than with sodium carbonate. With solutions of approximately equivalent sodium concentration, sodium carbonate (24 gram per liter) caused the complete oxidation of levulose in 30 minutes at 60° C. while sodium hydrogen phos-



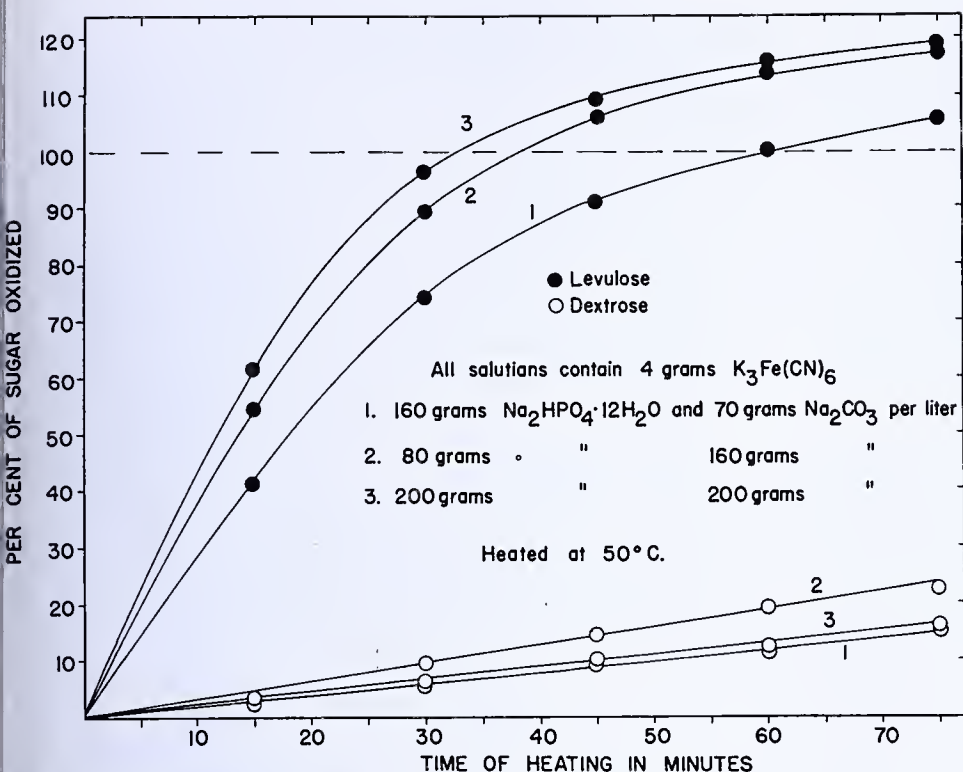


FIGURE 6. EFFECT OF CARBONATE AND PHOSPHATE CONCENTRATIONS ON RATES OF OXIDATION AT 50° C.

TABLE VII. SUGAR OXIDIZED AT 50° C.

(With buffer solutions of various concentrations of Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O and Na <sub>2</sub> CO <sub>3</sub> )										
Time of heating Min.	80 Grams Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 160 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter		160 Grams Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 70 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter		160 Grams Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 160 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter		200 Grams Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 160 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter		250 Grams Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 150 Grams Na <sub>2</sub> CO <sub>3</sub> per Liter	
	Dex-trose %	Levu-lose %	Dex-trose %	Levu-lose %	Dex-trose %	Levu-lose %	Dex-trose %	Levu-lose %	Dex-trose %	Levu-lose %
15	..	54.5	2.7	41.4	3.9	56.1	3.3	61.4	3.2	57.6
30	9.1	89.7	5.8	74.1	6.5	88.5	6.3	96.7	5.4	92.2
45	14.6	106.5	9.3	91.0	9.7	103.7	10.1	109.1	10.0	108.5
60	19.9	114.0	11.6	100.5	13.3	108.5	12.7	116.2	11.9	117.0
75	22.9	117.5	15.3	106.0	16.9	109.0	15.5	119.2	14.0	124.0

phate (80 grams per liter) required 160 minutes at 80° C. No pH measurements were made on the solutions, but this factor is being studied at the present time.

In every case in which phosphate was present, either by itself or in conjunction with carbonate, the course of the dextrose oxidation was, within experimental error, a linear function. This was not characteristic of levulose, either because the levulose was oxidized so rapidly that the straight portion of the curve occurred between the origin and the first point on the graph, or because of some unique property of the phosphate ion. When no phosphate was present, the dextrose graph was always a curved line similar in shape to the levulose curve. There can be no question that the phosphate ion does have a very characteristic action on the relative rates of oxidation of these two sugars.

When the carbonate and phosphate are used together, the effect is more complex and it is rather difficult to attribute any definite action to either one. However, a comparison of the figures for the rate of reaction in a solution containing only carbonate with the rate in solutions of the same carbonate concentration, but containing phosphate in addition, shows that the specific action applies largely to the dextrose. In other words, the rate of levulose oxidation in a solution of given carbonate concentration is practically the same whether phosphate is present or not, while the rate of oxidation of dextrose is dependent upon both. Thus, the effect of in-

creasing the carbonate concentration is to increase the rate of reaction for both sugars, while the effect of increasing the phosphate is to inhibit the oxidation of dextrose without markedly changing the rate of levulose reaction. A comparison of the data in Tables I and VI, and in III and VI, and a study of Table VII will bear this out. It appears from this that the most efficient oxidizing reagent for the selective determination of levulose is one of the highest possible phosphate and carbonate concentration—the carbonate to decrease the time of reaction and the phosphate to inhibit the oxidation of dextrose. The practicable limits are, of course, governed by the solubility of the salts and the difficulty encountered in acidifying a concentrated carbonate solution. The possibility of avoiding this inconvenience by the use of some reagent other than sodium carbonate is being studied in conjunction with the pH effect.

## Summary

When anhydrous sodium carbonate is used as the alkalizing agent, increasing the carbonate concentration increases proportionally the rate of oxidation of dextrose and levulose by an alkaline potassium ferricyanide solution.

An alkaline buffer of sodium monohydrogen phosphate dodecahydrate causes a very slow reaction for both sugars but inhibits the dextrose reaction more than the levulose.

Combining both carbonate and phosphate in the buffer causes an effect which is essentially a composite of the two individual effects—that is, carbonate accelerates the reaction rate of levulose while phosphate retards the oxidation of dextrose.

In all cases, increasing the temperature causes a proportional increase in the rate of oxidation of both sugars.

The alkaline potassium ferricyanide reagent containing both sodium carbonate and sodium hydrogen phosphate is a much better oxidizing agent for the determination of levulose in the presence of dextrose than the reagent composed of either one alone.

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# Determining Carbon Dioxide

## A Rapid Turbidimetric Method

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THE present method was developed primarily for determining traces of carbon dioxide in certain acid-soluble silicates. However, since amounts of carbon dioxide up to 10 mg. are determinable, the method is applicable to substances in which carbon dioxide is an abundant constituent as in carbonates. It is also applicable to the determination of free or combined carbon by wet combustion, but here, as also when sulfites, thiosulfites, or nitrites are present, decomposition of the sample must be made with chromic-sulfuric acid, and a chromic acid absorber interposed, in the manner illustrated by Scott (6).

The gravimetric determination ( $\mathcal{S}$ ) of carbon dioxide, while accurate, requires elimination of all traces of water vapor and is lengthy. For very small quantities, a microgravimetric technique would have to be employed.

The change in electrical conductivity (1, 5) caused by absorption of carbon dioxide in an alkaline medium requires elaborate apparatus and considerable precaution.

The use of the Van Slyke manometric apparatus (2) yields good results, even when small amounts of carbon dioxide are determined. The apparatus and procedure are, however, specialized, and the method is associated with dissolved carbon dioxide rather than insoluble carbonates. The reproducibility is given (2) as 1 per cent. A modified volumetric Van Slyke method (7) has been described in which acid may be used to liberate the carbon dioxide.

The titration of unprecipitated absorbent barium hydroxide

is simple in principle. When small amounts of carbon dioxide are to be determined, the barium hydroxide solution has to be dilute in order that the titer be accurate. Partridge and Schroeder (4) employ a carefully measured 0.02 *N* solution ( $1/_{25}$  saturated, 1 cc. equivalent to 0.44 mg. of carbon dioxide). At this dilution it appears that the carbon dioxide is not well absorbed, and a cumbersome scrubbing tower or a recirculation of the carbon dioxide-air mixture by pumping is resorted to.

The pH of an absorbent solution of sodium hydroxide containing phenolphthalein may be measured (9). As in titration, the solution needs to be dilute, and, in addition, at a predetermined concentration that varies with the amount of carbon dioxide to be absorbed.

## Apparatus and Procedure

The present description is that of the apparatus and procedure arrived at after numerous developmental experiments. In principle, the carbonate is decomposed with boiling acid, most of the water vapor condensed out, and the liberated carbon dioxide flushed out with air into absorbent barium hydroxide solution. The turbidity of the latter after correction for blank is a measure of the amount of carbon dioxide.

In Figure 1, *A* is a wide-mouthed extraction flask of 150-cc. capacity which contains the sample. This flask is fitted with a three-hole stopper through which pass thermometer *T*, acid-dropping funnel, *F*, and air inlet tube *I*. Air at low pressure

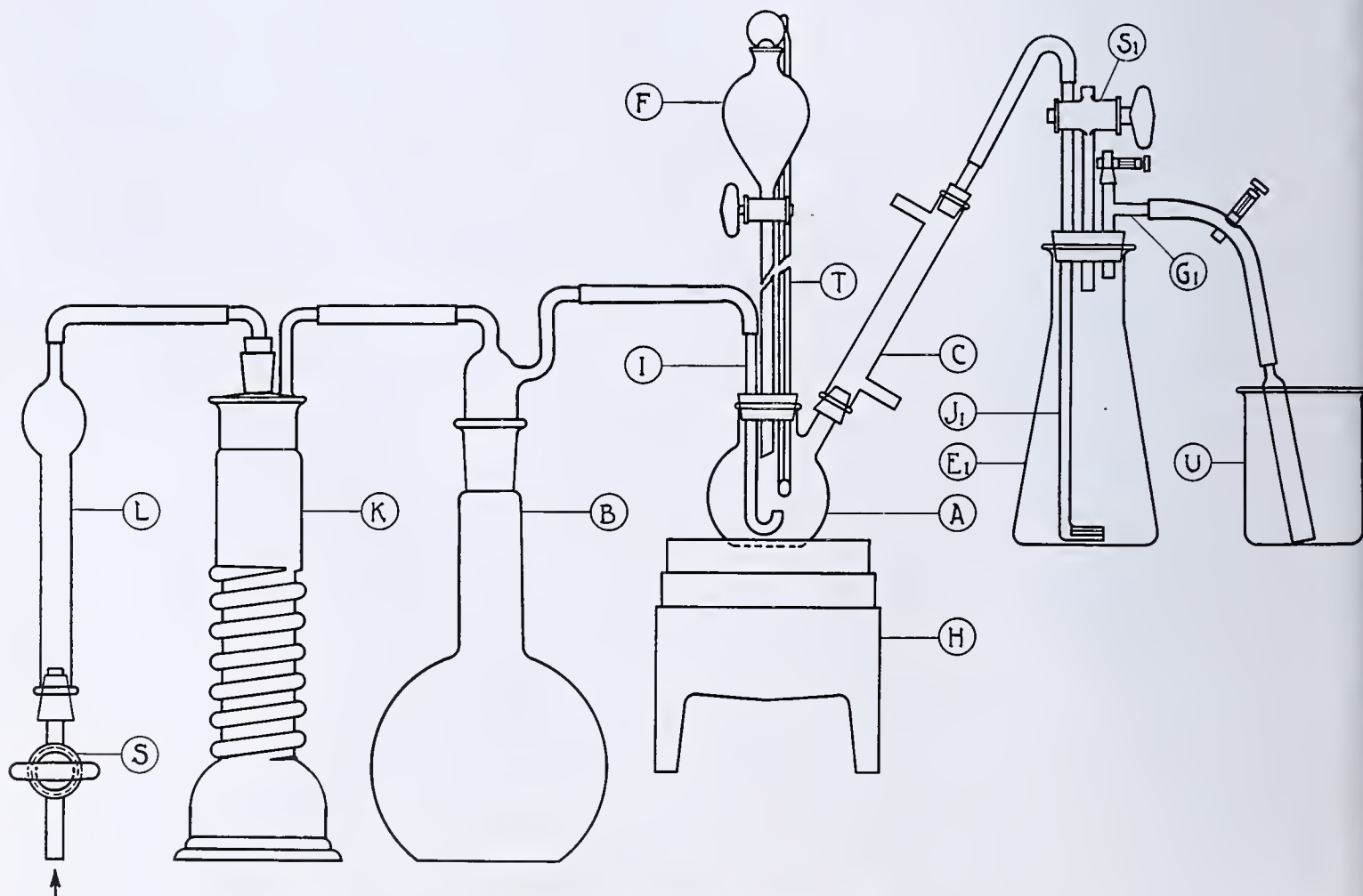


FIGURE 1. DIAGRAM OF APPARATUS



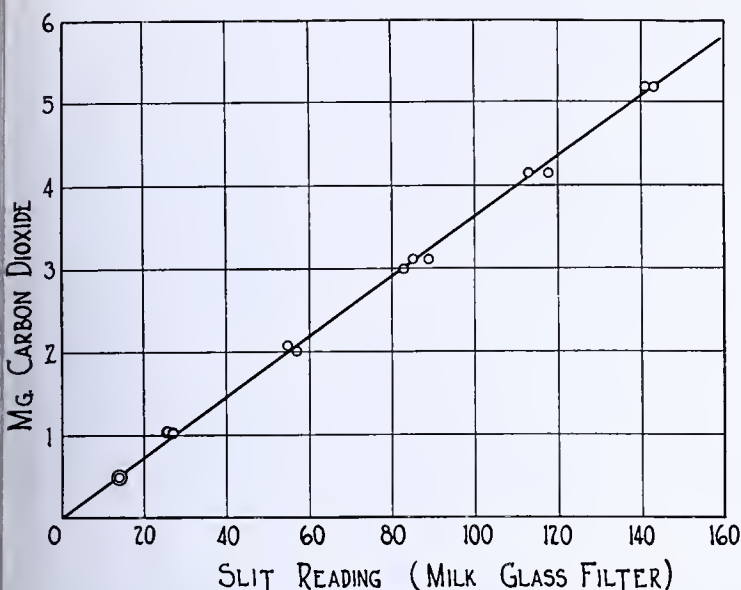


FIGURE 2. CALIBRATION AND PRECISION OF MEASUREMENT

(about 5 cm. of mercury), entering through *I*, is freed of carbon dioxide by passing it successively through soda lime in tube *L*, 33 per cent potassium hydroxide solution in *K*, and saturated barium hydroxide solution in *B*. The rate of flow is regulated by stopcock *S* backed by an open or shut valve and is estimated by bubble counter *U* at the end of the train. The bubble counter also serves as a seal.

The inner tube of condenser *C*, which is fused to flask *A*, is 6 mm. in inside diameter and the jacket is 14 mm. in inside diameter and 21 cm. long. Primary gas absorber *E*<sub>1</sub> is a 400-cc. wide-mouthed Erlenmeyer flask into which gas-washing tube *J*<sub>1</sub> passes through a three-hole stopper. A second similar absorber may be placed in series with *E*<sub>1</sub> as a check on the completeness of the absorption. This was actually done, but after conditions had been fully standardized the second absorber was discarded.

In making an experiment, the weighed or measured sample is first placed in flask *A*, a two-hole rubber stopper inserted therein, and well-stored boiled water pumped over until flask *A* is about two-thirds full. Approximately 300 cc. of filtered 50 per cent saturated barium hydroxide solution are pumped from a large reservoir into absorber *E*<sub>1</sub> by way of connection *G*<sub>1</sub>. After *E*<sub>1</sub> is filled, stopcock *S*<sub>1</sub> and the screw clamp on *G*<sub>1</sub> are closed.

About 10 cc. of concentrated hydrochloric acid are run from dropping funnel *F* into flask *A*. Heater *H*, which has previously been raised to temperature with all resistance out, is lifted up under flask *A*. At the same time, the air flow, adjusted to about 120 cc. per minute, is started. With a 550-watt heater, it takes about 4 minutes for the solution in the flask to reach boiling (temperature near 100°). After boiling has begun, a resistance is put in series with the heater to give an even rate of ebullition.

After 6 minutes of boiling, the heater is lowered and the air flow stopped. Part of the suspension in absorber *E*<sub>1</sub> is immediately transferred to the turbidimeter measuring cup, the latter is covered, and a turbidity reading is immediately made. If the suspension stays more than 2 or 3 minutes in the cup, the apparent turbidity is diminished, but the original reading is restored by shaking the suspension. Readings are unreliable after about 15 minutes.

After an experiment, the turbidimeter cup, flasks, and gas-washing tube are rinsed with dilute acid and with water.

The authors have used a Hellige turbidimeter, which has been described elsewhere (8). In this instrument the annular field produced by perpendicularly scattered light is matched against the circular field of a standard light source placed in front of a graduated adjustable slit. The instrument is in reality a nephelometer (9). Its particular advantage for the authors' work was the fact that it yielded a straight-line calibration curve.

### Blank Correction

The authors have found it necessary to run a blank experiment for each newly prepared stock solution of barium hydroxide, preferably once a day. While necessary, it is also advantageous to run such a blank experiment because certain refinements, such as flushing out the system with carbon dioxide-free air before an actual experiment, are then not

usually required. The turbidimeter reading of the blank is subtracted from the reading of the unknown.

An appreciable turbidity is shown even by fresh barium hydroxide stock solution. This is less than that of the blank.

TABLE I. CARBON DIOXIDE VALUES  
(Concentration of Ba(OH)<sub>2</sub> in per cent of saturation)

	20%		50%		90%	
	Stock soln.	Blank	Stock soln.	Blank	Stock soln.	Blank
Smallest value, mg.	0.47	0.58	0.62	0.69	0.40	0.47
Greatest value, mg.	..	0.87	0.91	1.02	0.91	1.09
Mean of all results, mg.	0.58	0.73	0.76	0.84	0.62	0.84
Av. fluctuation of the mean	0.07	0.07	0.11	0.10	0.14	0.12

The carbon dioxide values of different stock solutions and of the experimental blanks for a large number of experiments are shown in Table I. The turbidity of the different stock solutions ranges between 0.47 and 1.09 mg. of carbon dioxide and averages 0.8 mg. The turbidity of the blank averages 0.95 mg., so that the increment of turbidity originating in the experiment proper is relatively small, only 0.15 mg.

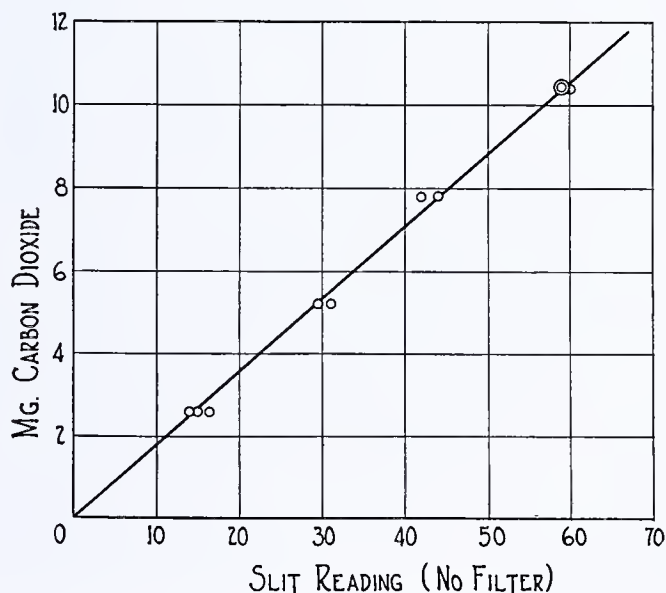


FIGURE 3. CALIBRATION AND PRECISION OF MEASUREMENT

Table I indicates that the average turbidity of stock solutions ranging in concentration between 25 and 90 per cent saturation, or of the corresponding blank, is the same, but the fluctuation in turbidity appears to increase slightly as one passes from the more dilute to the more concentrated solutions.

### Calibration and Precision of Measurement

Calibration and estimation of precision were carried out by analyzing known quantities of a volumetrically standardized sodium carbonate solution. For amounts of carbon dioxide between 0.5 and 5 mg. a milk-glass filter was used in the turbidimeter, while for amounts between 2.5 and 10 mg. of carbon dioxide no filter was used. The liquid depth of the turbidimeter cup was at all times 20 mm. A smaller quantity of carbon dioxide than 0.5 mg. may be determined expediently by changing the filter, the liquid depth, and the volume of absorbent barium hydroxide. However, the authors' problem did not require ascertaining appreciably smaller amounts of carbon dioxide than 0.5 mg.

Figures 2 and 3 represent a plot of the known milligrams of carbon dioxide against the slit reading of the turbidimeter (corrected for the blank in each experiment). It is observed



that a straight-line calibration curve is obtained that passes through the origin. By the method of least squares, the equation to the line obtained when the milk-glass filter is used is  $\text{mg. of CO}_2 = 0.0364 s$ , and to the line obtained in the absence of any filter,  $\text{mg. of CO}_2 = 0.176 s$ . The absence of a constant term in these equations proves that the line passes through the origin of coordinates.

TABLE II. CALIBRATION OF TURBIDIMETER

[Using known amounts of sodium carbonate solution. Comparison of  $\text{CO}_2$  introduced,  $[\text{CO}_2]_i$ , and  $\text{CO}_2$  calculated from calibration curve  $[\text{CO}_2]_c$ ]

Slit Opening Mm.	$[\text{CO}_2]_i$ Mg.	$[\text{CO}_2]_c$ Mg.	$[\text{CO}_2]_c - [\text{CO}_2]_i$ Mg.	Difference %
Milk filter in turbidimeter				
14	0.50	0.51	0.01	2.0
14	0.50	0.51	0.01	2.0
26	1.04	0.95	-0.09	-8.6
27	1.04	0.98	-0.06	-5.2
57	2.00	2.07	0.07	3.5
56	2.08	2.04	-0.04	-1.9
83	3.00	3.02	0.02	0.7
85	3.12	3.09	-0.03	-1.0
89	3.12	3.24	0.12	3.8
113	4.16	4.11	-0.05	-1.2
118	4.16	4.29	0.13	3.1
141	5.20	5.13	-0.07	-1.4
143	5.20	5.20	0.00	0.0
		Av.	$\pm 0.05$	$\pm 2.6$
		Probable error	$\pm 0.05$	$\pm 2.4$
No filter in turbidimeter				
14	2.60	2.46	-0.14	-5.4
16.5	2.60	2.90	0.30	11.5
15.0	2.60	2.63	0.03	1.2
29.5	5.20	5.18	-0.02	-0.4
31.0	5.20	5.45	0.25	4.8
42	7.80	7.38	-0.42	-5.4
44	7.80	7.73	-0.07	-0.9
59	10.4	10.4	0.0	0.0
59	10.4	10.4	0.0	0.0
60	10.4	10.6	0.2	2.0
		Av.	$\pm 0.12$	$\pm 3.2$
		Probable error	$\pm 0.11$	$\pm 2.7$

Table II gives in the first two columns the data by which the calibration curves were constructed. In the third column are shown the values of carbon dioxide estimated from the calibration curve, and in the last two columns the difference between the known and estimated values of carbon dioxide. In the range of concentration up to 5 mg. of carbon dioxide the average error is  $\pm 0.05$  mg. of carbon dioxide or  $\pm 2.6$  per cent, and in the range up to 10 mg. the average error is  $\pm 0.12$  mg. or  $\pm 3.2$  per cent. The probable errors calculated by the usual formula are somewhat less,  $\pm 2.4$  and  $\pm 2.7$  per cent, respectively.

TABLE III. PRECISION OF TURBIDIMETER

Slit Opening Mm.	Probable Error Mm.	%
28.5	0.32	1.1
47	1.37	2.9
92	1.88	2.0
173	3.65	2.1
	Av.	$\pm 2.0$

Part of these errors are attributable to the error of the method proper, and part to the error of the turbidimeter. The precision of the latter was ascertained by taking four readings for each of the different suspensions of barium sulfate and estimating the probable error in each case. Table III shows that the probable error of reading the turbidimeter averages  $\pm 2.0$  per cent. When this is compared with an average probable error of  $\pm 2.4$  and  $\pm 2.7$  per cent for the experimental result, it becomes evident that the major error of the experiment is due to error of reading the turbidimeter, and only a small part of the error is attributable to the method proper. In other words, the accuracy of the method is limited by the precision of the turbidimeter.

### Standardization of the Method

Standardization of the method required evaluation of the following conditions: Concentration of barium hydroxide, rate of air flow, time of boiling, and nature of the acid.

If the concentration of barium hydroxide is too low or the rate of air flow too high, absorption may not be complete. To test these factors, a second absorber was placed in series after the first absorber and the turbidity of the second absorber compared with that of a blank. The completeness of absorption by the first absorber was estimated by comparing the turbidity of the second absorber, expressed in milligrams of carbon dioxide, with that of a corresponding blank. Table IV shows that the difference of turbidity between the second absorber and the blank, even under drastic conditions of air flow, is no greater than that of the error of the blank and is about the same whether the concentration of barium hydroxide is 20 or 90 per cent. The authors have therefore chosen as standard a barium hydroxide concentration of about 50 per cent saturated, this being convenient, sparing of barium hydroxide, and safe, and have concluded that an air flow of even 300 cc. per minute is not too rapid.

TABLE IV. EFFECT OF RATE OF AIR FLOW AND OF DEGREE OF SATURATION OF BARIUM HYDROXIDE ON COMPLETENESS OF ABSORPTION OF CARBON DIOXIDE

CO <sub>2</sub> Sample Mg.	Air Flow Cc./min.	CO <sub>2</sub> , 20% Saturation Second absorber Mg.	Blank Mg.	Difference Mg.	CO <sub>2</sub> , 90% Saturation Second absorber Mg.	Blank Mg.	Difference Mg.
1	200	0.66	0.62	0.04	0.62	0.62	0.00
1	300	0.66	0.62	0.04	0.73	0.65	0.08
10	200	0.91	0.98	-0.07	0.91	0.80	0.11
10	300	0.80	0.70	0.10	0.91	0.80	0.11

If the air flow is not rapid enough and the time of boiling too short, evolution of carbon dioxide may be incomplete. A series of experiments was therefore made in which these factors were simultaneously varied. In Table V the values in parentheses are those in which manifestly the carbon dioxide had not been completely evolved. It may be concluded that a 1-minute time of boiling is inadequate even at a high rate of air flow and a 25-cc. per minute rate of air flow is inadequate even at a long time of boiling. The authors have chosen as safe a rate of air flow of 120 cc. per minute and a boiling time of 6 minutes.

TABLE V. EFFECT OF TIME OF BOILING AND RATE OF AIR FLOW ON COMPLETENESS OF EVOLUTION OF CARBON DIOXIDE FROM SAMPLE SOLUTION

Air Flow Cc./min.	Time of Boiling Min.	Sample Mg.	Carbon Dioxide Found Mg.	Difference Mg.
(70)	(1)	(1.00)	(0.63)	(-0.37)
(200)	(1)	(1.00)	(0.67)	(-0.33)
50	3	1.00	0.97	-0.03
200	3	1.00	1.09	+0.09
(25)	(6)	(1.00)	(0.61)	(-0.39)
50	6	1.00	0.98	-0.02
120	6	1.00	1.00	0.00
200	6	1.00	1.04	0.04
50	3	5.00	4.77	-0.23
120	3	5.00	4.80	-0.20
(25)	(6)	(5.00)	(4.11)	(-0.89)
50	6	5.00	4.84	-0.16
120	6	5.00	5.17	0.17

It is more satisfactory to use hydrochloric acid than sulfuric acid for evolution of the carbon dioxide, but one will suspect that some hydrochloric acid vapor might escape past the condenser. However, such hydrochloric acid as escaped would probably react with the excess barium hydroxide and so produce no effect on the suspension. The data of Table V show that the result is the same whether hydrochloric or sulfuric acid is used.

TABLE VI. EFFECT OF SUBSTITUTING SULFURIC FOR HYDROCHLORIC ACID

CO <sub>2</sub> in Sample Mg.	HCl Mg.	CO <sub>2</sub> Found H <sub>2</sub> SO <sub>4</sub> Mg.
1.00	0.98	0.98
2.08	2.04	2.33
4.16	4.11	4.01



### Summary

The turbidimetric method for determining carbon dioxide is simple and rapid. Only the sample and final suspension need to be measured accurately. The method can estimate carbon dioxide in amounts between 0.5 and 10 mg., but a smaller quantity than 0.5 mg. may also be determined. The average probable error is  $\pm 2.6$  per cent. Most of this error is associated with the precision of the turbidimeter which is about  $\pm 2.0$  per cent.

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## Effect of Various Pre-extractions on the Lignin Determination of Wood

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THE present methods for the determination of lignin in wood are subject to criticism because they cannot be applied alike to all types of material. The sulfuric acid method, which is favored by most analysts because it is simpler to perform and gives, under controlled conditions, more uniform results than other methods, is subject to the same criticism: Certain carbohydrates are converted into a water-insoluble material, which appears in the lignin residue if allowed to stand in contact with the sulfuric acid too long a time or at too high a temperature (6, 7, 10, 11). To overcome this objection and to make control of temperature unnecessary, several investigators (5, 8) have suggested that these unstable carbohydrates be removed by a preliminary extraction with hot dilute acid. They assumed that the easily hydrolyzable carbohydrates as determined by Hawley and Fleck (4) were the same as those which were responsible for the formation of the insoluble ligninlike residue. Campbell and Bamford (1) contend that preliminary treatment

causes a polymerization of some carbohydrate substance with an increase in lignin yield.

Work on this aspect of the analysis of lignin has been in progress at the Forest Products Laboratory at Madison, Wis., for several years. Preliminary extraction with organic solvents, cold water, hot water, dilute sodium hydroxide, barium hydroxide, sodium carbonate, sodium sulfite, and dilute hydrochloric, dilute sulfuric, and 3 per cent oxalic acid have been tried and, in addition, various concentrations of dilute sulfuric acid under pressure. The work with sodium hydroxide on sugar maple sawdust was reported by Harris (3), various treatments with hot and cold water and organic solvents by Ritter and Barbour (9), and some of the work showing the effect of 3 per cent sulfuric acid on sugar maple sawdust by Cohen and Harris (2).

This report contains, in table form, the results of further work with sulfuric acid and of various other pretreatments on wood.

TABLE I. EFFECT OF ACID PRE-EXTRACTION ON SPRUCE AND MAPLE WOOD

Wood Treatment	Total Time of Treatment Hours	Alcohol-Benzene-Water Extrac- tives <sup>a</sup> %	Loss by Treat- ment <sup>a</sup> %	Lignin Content <sup>a</sup> %	MeO in Wood <sup>a</sup> %	MeO in Lignin <sup>b</sup> %	Calculated Loss of Lignin <sup>a,c</sup> %
1. Spruce extracted with alcohol-benzene and cold water	3	4.3	..	27.47	..	16.6	..
2. No. 1 + 3 hours on boiling water bath with 3% sulfuric acid	6	..	24.0	26.4	6.46	16.5	3.65
3. No. 2 + 3 hours with 3% sulfuric acid	6	..	28.0	25.5	6.25	16.4	6.95
4. No. 3 + 3 hours with 3% sulfuric acid	9	..	30.2	24.9	5.87	15.1	9.5
5. No. 4 + 3 hours with 3% sulfuric acid	12	..	33.9	23.7	5.34	15.0	13.9
6. No. 5 + 6 hours with 3% sulfuric acid	18	..	37.0	22.9	4.95	14.8	16.8
7. Spruce + 3 hours with 3% oxalic acid	3	..	16.65	26.1	..	16.5	4.7
8. No. 7 spruce + 3 hours with 3% oxalic acid	6	..	24.2	24.0	..	16.4	11.5
9. No. 8 + 3 hours with 3% oxalic acid	9	..	28.4	23.7	..	16.4	13.9
10. No. 9 + 3 hours with 3% oxalic acid	12	..	28.7	23.7	..	16.0	..
11. No. 10 + 6 hours with 3% oxalic acid	18	..	29.0	23.7	..	15.9	..
12. Maple extracted with alcohol-benzene and water	..	4.07	4.07	22.75	..	20.4	..
13. No. 12 + 4 hours' boiling with 1% sulfuric acid	4	..	23.0	19.85	..	20.5	12.2
14. No. 12 + 1 hour's boiling with 3% sulfuric acid	1	..	26.7	19.10	..	20.3	16.0
15. No. 12 + 4 hours' boiling with 3% sulfuric acid	4	..	36.4	17.6	..	20.2	22.5
16. No. 12 + 6 hours' boiling with 3% sulfuric acid	6	..	34.8	17.75	..	20.0	22.0
17. No. 12 + 3 hours' boiling with 3% oxalic acid	3	..	25.5	20.3	6.60	20.3	10.5
18. No. 17 + 3 hours' boiling with 3% oxalic acid	6	..	31.5	18.5	5.95	20.4	18.5
19. No. 18 + 3 hours' boiling with 3% oxalic acid	9	..	32.6	18.3	5.48	20.3	19.5
20. No. 19 + 3 hours' boiling with 3% oxalic acid	12	..	36.0	17.4	5.40	20.5	23.5
21. No. 20 + 6 hours' boiling with 3% oxalic acid	18	..	38.0	16.9	5.40	20.0	25.5

<sup>a</sup> Percentages are calculated from unextracted oven-dried wood.

<sup>b</sup> Percentages based on isolated lignin.

<sup>c</sup> Loss of lignin (due to treatment)

Original lignin (after alcohol-benzene extraction)\*



TABLE II. EFFECT OF PRE-EXTRACTION WITH ACID, SALTS, AND ALKALI ON LIGNIN DETERMINATION OF MAPLE WOOD  
(On boiling water bath)

Treatment	Time Hours	Loss by Solvent Extraction %	Loss by Treatment %	Lignin Based on Original Wood %	MeO in Lignin %
Alcohol-benzene extraction	...	4.07	4.07	22.7	20.4
1% ammonium oxalate	4	..	2.4	22.5	20.5
2% ammonium oxalate	7	..	12.1	21.0	20.4
2% sodium sulfite	3	..	11.8	20.7	20.4
0.5% barium hydroxide	6	..	10.8	21.2	20.4
15% sulfuric acid	3	..	25.9	21.2	20.5
2% hydrochloric acid	3	..	24.3	19.4	20.3

TABLE III. EFFECT OF HYDROLYSIS ON LIGNIN AND CELLULOSE VALUES IN MAPLE WOOD

Treatment	120 Pounds' Pressure, 30 Minutes						135 Pounds' Pressure, 30 Minutes						150 Pounds' Pressure, 30 Minutes					
	Ex- peri- ment No.	Hy- dro- lyzed wood %	Cel- lu- lose <sup>a</sup> %	Lig- nin <sup>a</sup> %	Lig- nin <sup>b</sup> %	Meth- oxyl in lig- nin %	Ex- peri- ment No.	Hy- dro- lyzed wood %	Cel- lu- lose <sup>a</sup> %	Lig- nin <sup>a</sup> %	Lig- nin <sup>b</sup> %	Meth- oxyl in lig- nin %	Ex- peri- ment No.	Hy- dro- lyzed wood %	Cel- lu- lose <sup>a</sup> %	Lig- nin <sup>a</sup> %	Lig- nin <sup>b</sup> %	Meth- oxyl in lig- nin %
1% sulfuric acid	473	64.95	63.4	32.5	21.1	20.6	485	63.70	66.0	33.3	21.2	20.5	492	62.87	64.6	35.0	22.0	20.2
hydrolysis	474	62.30	61.9	36.2	22.5	20.3	486	61.83	63.0	37.1	22.9	20.2	493	60.52	61.6	38.5	23.3	..
2% acid	475	60.10	59.6	37.6	22.6	20.3	487	59.81	61.0	39.0	23.3	20.0	494	58.24	58.5	41.5	24.3	19.8
3% acid	476	58.95	57.1	39.8	23.4	20.0	488	58.74	58.5	41.1	24.1	19.5	495	57.20	55.4	44.6	25.6	..
4% acid	477	56.90	55.6	41.8	23.8	19.7	489	56.80	55.0	45.0	25.5	19.2	496	56.55	52.5	47.2	26.2	18.5
5% acid	..	..	..	..	..	..	490	55.72	54.4	45.4	25.6	18.9	497	54.03	49.4	50.0	27.3	..
6% acid	..	..	..	..	..	..	491	54.00	49.9	50.2	27.3	17.5	498	52.00	43.0	57.0	29.6	15.9
7% acid	484	54.18	52.0	46.6	25.4	18.4	..	..	..	..	..	..	..	..	..	..	..	..
Water	500	82.50	62.5	27.95	22.9	20.7	..	..	..	..	..	..	..	..	..	..	..	..
3% oxalic acid	499	68.37	63.0	33.6	22.9	20.7	..	..	..	..	..	..	..	..	..	..	..	..

<sup>a</sup> Per cent cellulose and lignin yields based on oven-dry residue after hydrolysis.

<sup>b</sup> Per cent lignin based on weight of original wood.

## Experimental Procedure

Sawdust obtained from sawing selected air-dried wood free from bark, knots, and compression wood, was cut to pass a 40-mesh screen in a Wiley mill and extracted successively with cold water, hot 95 per cent alcohol, hot alcohol-benzene mixture, followed by alcohol and then water, and finally dried in the air to 5.5 per cent moisture content.

Table I gives the data for the effect of successive treatments on a boiling water bath with 3 per cent sulfuric and oxalic acid, and also other individual treatments with sulfuric acid on spruce and maple sawdust. Table II shows the effect of various other materials at the temperature of the water bath. The furfural determination was omitted because, as shown by Cohen and Harris (2), practically all the furfural-forming material was destroyed by contact with acid. Five hundred cubic centimeters of the acid solution were used for the extraction of each 2 grams of wood. All extractions were carried out in groups of six for each series of extractions and the average of these was taken. The acid extract was filtered from the sawdust while hot, since cooling caused a precipitation of some of the dissolved material.

Table III gives the lignin and cellulose analytical values obtained upon maple wood after treatment at 8.436, 9.49, and 10.545 kg. per sq. cm. (120, 135, and 150 pounds per square inch) steam pressure in sulfuric acid at concentrations from 1 to 7 per cent, in water, and in 3 per cent oxalic acid.

## Discussion

Examination of Tables I and II shows that pretreatment of either softwood or hardwood with dilute sulfuric or oxalic acid removed lignin as well as carbohydrate material. Spruce wood, which had been extracted by six 3-hour treatments with 3 per cent sulfuric acid, lost 16.8 per cent of its lignin. (No record was made of the loss at the end of the fifth 3-hour treatment.) Three treatments with 3 per cent oxalic acid removed 13.9 per cent of the lignin from spruce. Filtrates from the extractions of spruce wood gave a precipitate that was soluble in glacial acetic acid, alcohol, and chloroform. The glacial acetic acid solution of this material was poured

into a large volume of water, which caused the material to precipitate again. This material contained 16.8 per cent of methoxyl and had properties that indicated that it was lignin.

Maple wood lost 22.5 per cent of the lignin when heated 4 hours with 3 per cent sulfuric acid. When the heating was continued for 6 hours, some of the lignin was again converted into an insoluble compound, since the loss is slightly less than with a 4-hour treatment. Oxalic acid, during six 3-hour treatments, removed 25.5 per cent of the lignin, which was more than that removed by the action of sulfuric acid (2). Material precipitated from the sulfuric and oxalic acid solutions on standing or on increasing the acid concentration

was dissolved in glacial acetic and reprecipitated by pouring into water. This material had the same methoxyl content (20.6 per cent) and other properties which indicated that it was lignin.

Treatment with ammonium oxalate had about the same effect on the lignin content as did extraction with water (see Table II). There was a slight loss of lignin.

Sodium sulfite solution also removed lignin from wood. This may be accounted for by the alkalinity of the solution. Barium hydroxide removed less because the barium derivative of lignin is insoluble.

Fifteen per cent sulfuric acid dissolved less lignin from wood than did 3 per cent, perhaps because the higher concentration depressed the solubility of the lignin.

Hydrochloric acid also had the property of removing lignin; the lignin content was lowered almost 15 per cent by treatment with 2 per cent acid for 3 hours at 90° C.

When the hydrolysis took place under pressure, as shown in Table III, a loss of lignin was observed at the lower concentrations of acid and lower pressures. Increase in acid and increase in pressure caused a reprecipitation of some of the lignin and also the conversion of some of the carbohydrates into a ligninlike residue that was isolated with the lignin and, consequently, gave a residue with a low methoxyl content.

This work shows lignin to be soluble in dilute acid solutions. It may be precipitated by long heating, heating under pressure, or increasing the acid concentration. Extraction of lignin-containing material with 3 per cent acid, sodium sulfite, and other salts or bases removes lignin and should be avoided if an accurate determination of the lignin content of a sample of wood is desired.

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## Testing Dentifrice Abrasives

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CONSIDERABLE emphasis is now placed on the physical properties of the insoluble materials that are almost universally used in dentifrices to assist the brush in cleaning the tooth surface. This close attention was stimulated because certain dentifrices were considered unduly abrasive, while a number of scattered observations on the effect of brushing extracted teeth with commercial dentifrices (6) indicated a danger of damage to the various tooth structures resulting from daily use over a period of years. It has, moreover, been shown recently (2, 11) that although wear of the enamel is very slight with the majority of dentifrices in use today, the softer tissues exposed by gum recession are much more open to attack.

Consequently it is important to have a means of testing the abrasiveness of fine powders. Such tests are necessary or control in choosing suitable types of powder bases and for testing finished dentifrices in order to exclude those having excessive abrasive effects. For these routine purposes biological surfaces that are variable and require tiresome repetition in the test are obviously unsuitable and some standard surface is essential. Several instruments have been described which measure the abrasiveness of fine powders in arbitrary units against such surfaces, but so far their readings have not been standardized in terms of powders of characteristic physical properties nor have the abrasivenesses of the powders tested been related to the amount of wear produced by them on tooth structures.

A systematic study should aim first at grading a series of defined powders on the abrasion apparatus and then attempting to establish limits of particle size and hardness—the two important characteristics involved—liable to cause serious damage to the several tooth structures involved. In this connection Ray and Chaden (6) have pointed out that different individuals probably require dentifrices of different abrasiveness.

An experimental approach of this type is simple when one considers a single substance, since it is self-evident that the grading order of a series showing increasing particle size must be the same against all surfaces. (The actual range of abrasiveness of the series will, of course, vary with the different surfaces according to the degree of penetration of the particles.) Difficulty must, however, be anticipated in comparing chemically different powders. Thus a series of samples each containing the same number of identically sized particles could conceivably be graded in different orders by different surfaces because of the specific interaction of the physical factors involved, such as hardness, particle shape, ductility, etc. At the same time it should be possible to assess different powders closely enough for practical purposes, especially as the range of hardness and particle size likely to be used is small.

### Grading of Fine Abrasive Powders

**SCRATCH versus ABRASION TEST.** The effect of the abrasive can be estimated either by examining the scratches left on the surface after a small amount of rubbing or by continuing the treatment until a measurable amount of the surface has been removed. The two methods are complementary, each having certain advantages. The scratch test is selective, different sized scratches being made by different particles (8), and is ideal for finding small amounts of added adulterant such as pumice or emery. Even the very simple form of test described in Federal Specification FFF.D.191 for dentifrices is fairly sensitive (10).

The abrasion test gives a quantitative figure for the amount of abrasion but it is not possible to distinguish scratches of different depth. For the purpose of grading powders, however, a quantitative abrasion test is essential, though discrimination must be used in assessing the results when hetero-disperse powders are being tested.

Experimentally considerable difficulty is involved in these tests, as may be appreciated by the experience of Souder and Schoonover (10) who found with a rotating table test that "the addition of 10 per cent of fine emery to a paste of minimum abrasiveness did not increase appreciably the loss in weight of the disk." The apparatus of Ray and Chaden (6) is, however, very sensitive, while the modification with glass bed (8) can distinguish an addition of 0.020 gram per cent of a coarse ingredient in a fine dentifrice. Incidentally, the explanation of Souder and Schoonover that "a film of soap or some other ingredient prevents the two surfaces coming together" is not tenable, since results have been obtained in substantial agreement in comparing powders alone and made up in commercial dentifrices.

In previous work on grading the powders have not been sufficiently characterized and the reason for the wide variation in tests with different samples does not appear. Thus Ray and Chaden using commercial dentifrices found figures for calcium carbonate from 1.5 to 10 (milligrams of weight loss from an antimony block after 5,000 revolutions) and for calcium phosphates from 0.7 to 17, and these differences are presumably due to differences in particle size distribution and the presence of impurities. For the results, however, to have more than a restricted value referring to the particular sample, each series should be characterized from this point of view. Wright and Fenske (11) gave ranges of a similar order (with the same apparatus) using powders, but again no physical description was attempted.

An earlier communication (8) described tests on a series of experimentally precipitated chalk powders by which a relation between particle size and abrasiveness was established.



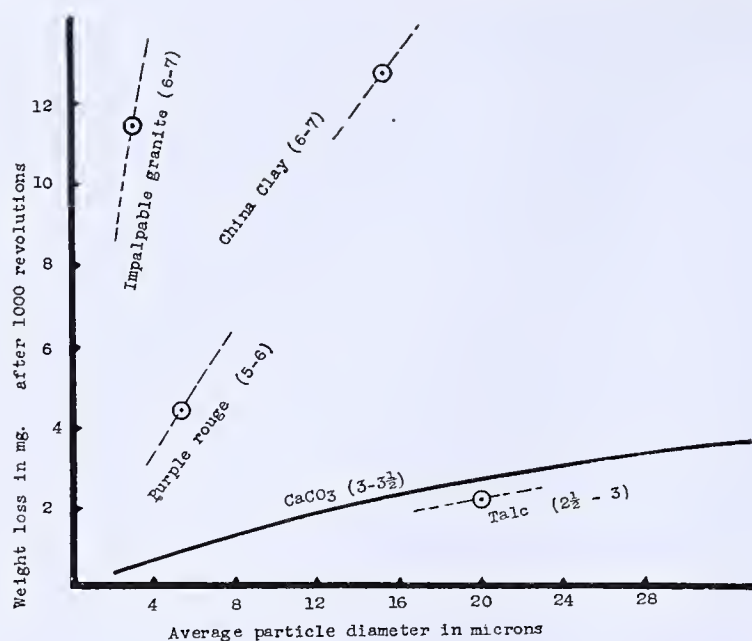


FIGURE 1. ABRASIVENESS OF SIZED POWDERS MEASURED WITH ANTIMONY PLATE ABRASION APPARATUS

Dotted lines indicate probable curves based on analogy with calcium carbonate series which has been studied in detail. Figures in brackets are approximate Mohs hardnesses of the different materials.

Hardness was also shown to be extremely important where very hard particles such as those of the abrasive industry are concerned but of much less importance with the usual run of dentifrice abrasives whose hardness has the small range of 2 to 3.5 on the Mohs scale. Figure 1 shows the general character of the results, but only the calcium carbonate series was investigated in detail since homodisperse sized samples of other materials were not available.

It is evident that small increments of particle size are much more important with the harder than with the softer powders. The curve for precipitated chalk is of interest, showing that the abrasive effect of built-up aggregates is less for a given particle size than that of calcite rhombs, the difference being most marked with the finer size grades.

**ANTIMONY PLATE AS STANDARD ABRASIVE SURFACE.** An important consideration in a test involving the relative motion of solid surfaces is the possibility of surface flow. When comparing a series of powders of different abrasiveness the finer ones, since they renew the surface less rapidly, might allow an amorphous and more resistant layer to build up. Providing care is taken that the tests all refer to the surface in a standard condition, this would merely alter slightly the relative abrasiveness of the coarse and fine powders on the arbitrary scale used. Thus there would be a slightly different arbitrary scale in which, if the fine powders are taken as standard, the abrasiveness of the coarser ones would be exaggerated.

Antimony was originally chosen (6) as an abrasion standard because it has a hardness between that of enamel and dentine but approximating the latter (4). Other advantages which minimize the extent of surface flow are its brittleness and its high melting point (630° C.) for a metal of low hardness. [The experiments of Bowden and Hughes (1) have shown that the attainment of a local momentary temperature approaching the melting point plays an important part in the formation of the polish layer.] The conditions of the test will determine how rapidly such surface temperatures are reached. In the apparatus described below the loading is 100 grams per sq. cm. and the relative speed 42 cm. per second; as the test lasts only 10 minutes and there is ample lubrication the temperature rise should not be excessive. Thus, the conditions are such that little flow should occur. There is, however, a

tendency to a decrease of the abrasion values in successive runs, and to correct for this tendency and also for variation in other experimental conditions on different occasions such as the thickness of the film of suspension and setting of the plate, frequent checks are made with a standard powder and the results for the unknown "bracketed" with these figures. The antimony plate also is reground at intervals in a standard manner (rubbed down on a plate-glass sheet with successively fine grades of emery and finally with chalk, all in glycerol suspension).

**MODIFICATIONS IN ABRASION APPARATUS.** Since the original description was published (8), certain modifications have been made in the light of recent experience with the test which materially improve the ease of working.

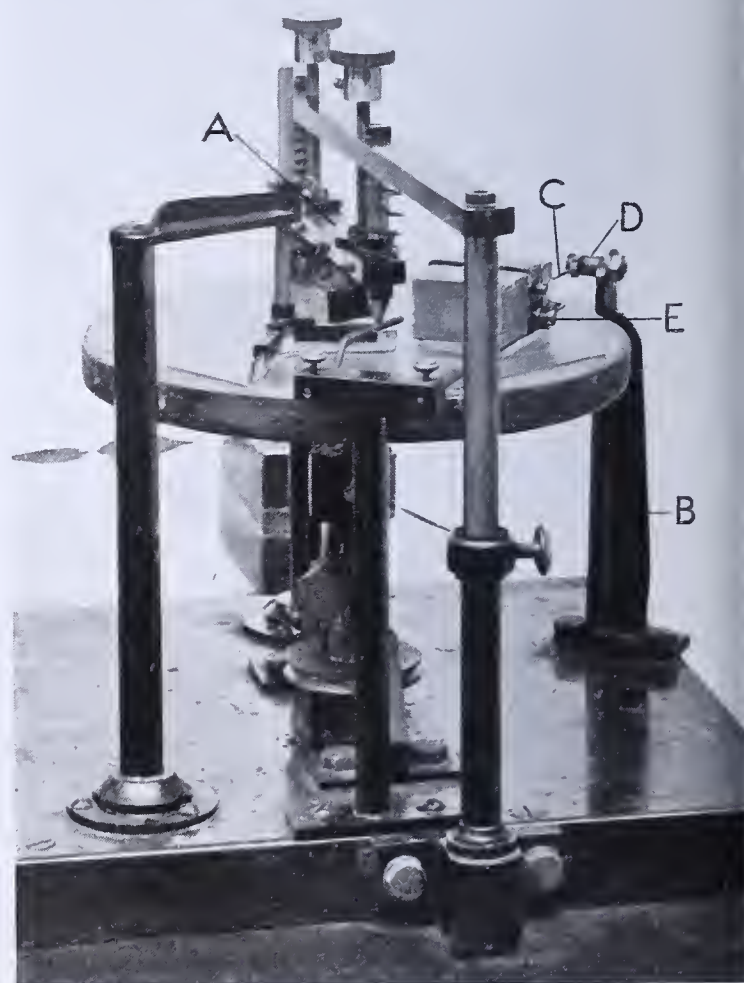


FIGURE 2. ANTIMONY PLATE ABRASION APPARATUS FOR FINE POWDERS

Modified form of apparatus as now used

Figure 2 shows that the spreader, A, has been made more rigid and controllable, so that the film of suspension can be set to a repeatable thickness. The position of the antimony plate on the glass bed is adjusted by means of the slotted holes at the base of the pillar, B. It is important that the trailing arm, C, should be horizontal (and thus parallel to the glass surface) and this is set by the slot at the pillar pivot, D. The stirrup pivots, E, and the lead block should be on a diameter of the bed. These adjustments are made until the abrasion over the whole surface of the antimony plate is uniform as judged visually after a few hundred revolutions. Differences between the leading and trailing edges of the plate are corrected by altering the position of the pillar pivot, C; differences between the two sides by adjusting the spreader screws, or, possibly, altering the set of the glass bed. Streaks of no abrasion on the plate are due to bumps in the rubber spreader and may be smoothed away with sandpaper.

The speed of rotation has now been standardized at 80 r. p. m. during a test which lasts for 1000 revolutions. The individual tests are repeatable to within about 20 per cent.



### Influence of Particle Size on Abrasion

Miller (5) on the basis of hand-brushing experiments stated that three different sizes (unspecified) of calcium carbonate had similar abrasiveness. This can, however, apply only to a very limited particle size range or to sizes above a certain minimum, since there must be a decreasing abrasiveness with smaller sizes; in the limit, colloid particles can have no possible abrasive action. Further, from the nature of the abrasion process such a relation must be a pure coincidence. On the other hand, the character of the backing or bed has an important effect on abrasiveness, the use of a hard bed of glass exaggerating the abrasive effect of the coarser and harder particles especially. This is a useful feature from the point of view of grading powders, as it provides a more stringent and sensitive test. Two hard surfaces (nickel-copper alloy and glass) are used in the federal test (10) for dentifrices.

Consideration of the mechanism of abrasion shows that even were the gross abrasion loss per given weight of powder independent of particle size, the condition approximated with a soft bed, the actual scratch depth must increase considerably to compensate for the decreased number of particles—i. e., it is necessary to consider both particle size and abrasion in appraising the powder. Previously this has been overlooked.

The total abrasion loss depends on both the number and volume of the individual scratches. It is fair to assume that the number of these and hence the "total scratch length" are proportional to the number of particles per gram of material. Thus for two homodisperse powders with particles of diameter  $x$  and  $2x$  the abrasivenesses are proportional, respectively, to  $v_1/x^3$  and  $v_2/8x^3$  where  $v_1$  and  $v_2$  are the volumes of the scratches per unit length. For these quantities to be equal—i. e., for abrasion to be independent of particle size— $v_2$  must equal  $8v_1$ . Evidently the scratch must be much deeper in the case of the larger particles to fulfill this equality, the actual relation between scratch depth and volume depending on the assumed shape of the hollow and the fraction of the particle buried.

The simplest case is that of a cylindrical scratch which would be made by a spherical particle. Figure 3 shows the relative scratch volumes for two particles of radii  $x$  and  $2x$ , respectively. From the relation between the scratch depth,  $s$ , and the area of the segment,  $ABC$ , it is possible to calculate the scratch depths. For the condition of scratch depth independent of particle size (assuming  $s = x/20$ ) the scratch depth increases about 3.25 times when the particle size doubles; for the experimental figures quoted (8) the factor is 4.5. These ratios are a minimum, since the assumed penetration is probably too high under the experimental conditions concerned. Clearly, since scratch depth is an important factor in assessing the possible damage of a dentifrice abrasive, the particle size as well as the measured abrasion figure must be considered.

### Relation between Abrasiveness Determined against Antimony Plate and Wear on Tooth Structures

Having established a satisfactory means of grading powders, can the results be related to the wear of the teeth? Here the variability of the biological material provides the biggest difficulty, the enamel itself ranging in microhardness units from 330 to 2050 and the softer tissues from 85 to 165 (6). Thus there is no such thing as a standard tooth surface so an exact correlation cannot be expected.

A direct experimental comparison between the weight losses with the antimony block abrasion meter of Ray and

Chaden and the wear on tooth structures has recently been described by Wright and Fenske (11), using extracted teeth. Unfortunately, the powders they used were not characterized according to their physical properties, and the results lack the significance which they would have had if a few graded series of different powders had been compared. The authors also did not take sufficient account of the variation in their biological material and the experimental errors involved and concluded that the agreement was not good. However, a critical examination of their data (7) showed that if such variation was allowed for there was satisfactory agreement—i. e., the indication of the abrasion meter was a useful guide to the amount of wear produced in the average tooth structure.

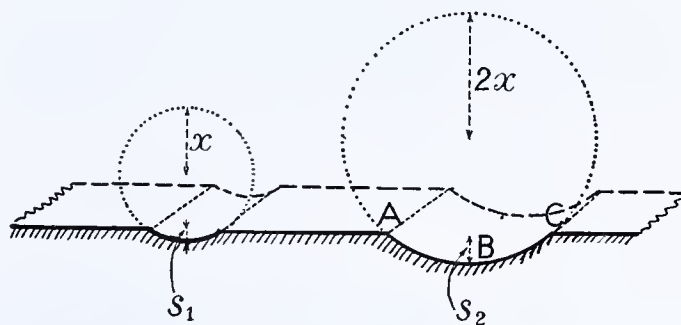


FIGURE 3. RELATIVE SCRATCH DEPTHS

For spherical particles with diameters in the ratio 1 to 2

It has been assumed that the wear on such extracted teeth parallels the wear that would occur with the same abrasive in the mouth. This seems reasonable for the surface enamel, though less sound for the softer tissues in which, as the experiments with radioactive indicators have shown, the interchange of ions is more frequent. Any closer correlation must involve clinical experience, although experiments with extracted teeth exaggerate considerably the degree of wear to be expected *in vivo*, because the extracted teeth lack the natural protective film which in the mouth is constantly reformed after cleaning. It is also known that the outermost layer of enamel is hypercalcified and so may act as an additional protective layer. Obviously in tests on extracted teeth in which some depth of tissue is removed, the abrasion measured is the mean for several successive layers of imperceptibly graded characteristics. (For these reasons the type of statement which equates so many strokes in an abrasion machine with the effect of a certain number of years of tooth cleaning must be viewed with caution.)

These considerations clearly will complicate the application of the abrasion results. However, the fact that Wright and Fenske found a reasonable correlation, taking the mean of 12 to 40 tests on different teeth, which probably vary in hardness to an extent overshadowing the effect of the protective layers, indicates that the tests with the antimony plate are of real significance to the probable wear *in vivo*. In any case the establishment of a standard of abrasion is essential and the measure of agreement obtained is distinctly encouraging support for the antimony plate grading of dentifrice powders.

On the basis of the tests with sized suspensions heterodispersity in the powder is a disadvantage from this point of view, since the effect is that the larger particles bear a disproportionate amount of the load and so bite more deeply, while the finer ones do little work. The depth of the cut required by each single particle should presumably be of the same order as the thickness of the mucin film investigated by Haeseler and co-workers (3, 9). This will be a very variable quantity, but when visible the film must have a minimum thickness of the order of 0.5 micron.



### Summary

In view of the possibility of damage, especially to the softer tissues, by regular brushing, a standard test for grading the fine powders used in dentifrices is important. An abrasion test is more satisfactory than a scratch test, although the latter is useful for detecting coarse adulterants and is more selective.

Antimony has several advantages as a standard surface. Surface flow does not appreciably interfere with the test, providing proper precautions are taken.

Some modifications of a convenient abrasion apparatus are described. Results obtained with this apparatus using sized powders show that particle size distribution is important, since for the same abrasion loss per unit weight of powder larger particles will give fewer but deeper scratches.

The measure of experimental agreement found by Wright and Fenske between the abrasion results with a variety of powders against the antimony surface and the tissues of ex-

tracted teeth is held to justify the use of the standard surface for testing dentifrices.

The correlation between the abrasion test on extracted teeth and the wear involved in cleaning of teeth *in vivo* is discussed. The test with extracted teeth exaggerates the wear.

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## A Simple Hydrogen Electrode Outfit

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A HYDROGEN electrode outfit capable of meeting established requirements for the accurate determination of the hydrogen-ion concentration of buffers is a frequent necessity in many types of work. The extensive use of glass electrodes has increased this need, because the absolute accuracy of the glass electrode technique is actually limited to the accuracy of the method used in standardizing the calibrating buffer (3).

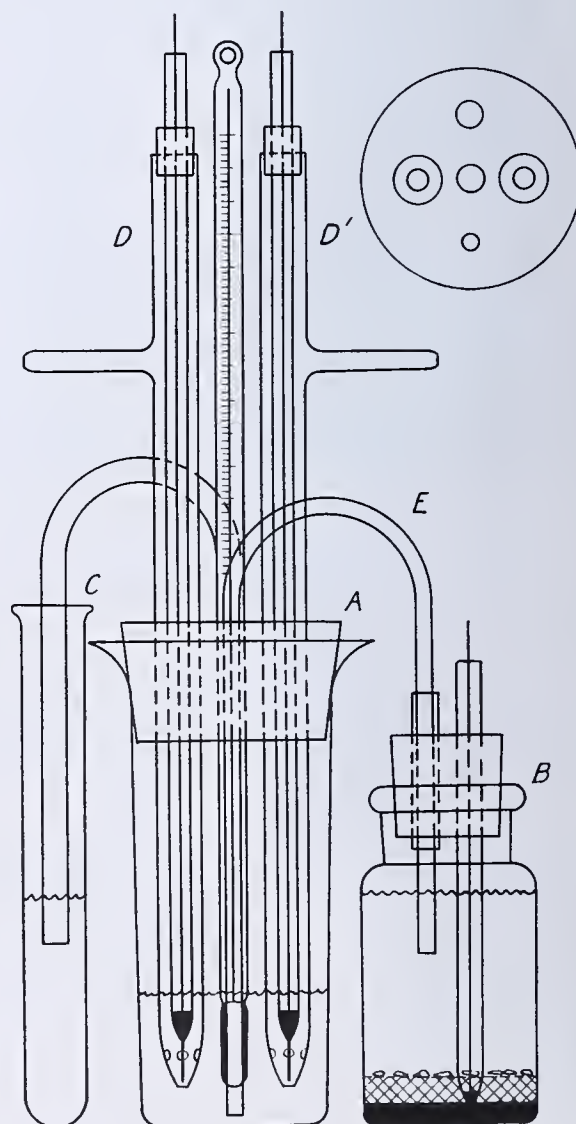
The apparatus shown in the accompanying sketch has been useful in checking buffers according to the criteria suggested by Beans and Hammett (1). It was constructed from the following pieces: A, 180-cc. electrolyzing beaker; B, 60-cc. wide-mouthed bottle; C, ordinary 12.5-cm. (5-inch) test tube. The two electrodes, D and D', are similar in design to the Wilson type. The saturated calomel half-cell, B, and agar gel salt bridge, E, were patterned after E. Müller's design described by Kolthoff and Furman (2). The trap, C, should be filled with water to about 1 cm. above the end of the tube leading into the electrode chamber. The electrode chamber is made gas-tight by fitting a short piece of rubber tubing around the salt bridge at the point where it leaves the chamber.

The position of the holes in the No. 10 rubber stopper is shown in the upper-right corner of the diagram.

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# Iodometric Determination of Copper

## Selection of a Suitable Buffer Solution

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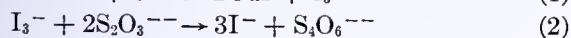
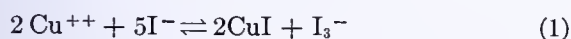
IN THE iodometric determination of copper the titration is usually performed in a buffer solution: (1) to keep the pH around 3 or less but high enough to cause the oxygen-iodide reaction to have a negligible rate; (2) if arsenic is present, to adjust the pH to a value between 3.2 and 4.0 to prevent an appreciable reaction between iodide and pentavalent arsenic. The buffer solutions used for such purposes should be those of acids with suitable ionization constants and those in which the cupric ions do not form insoluble, weakly ionized, or complex compounds to too great an extent.

In determining copper in solutions containing iron and arsenic, Park (4) used a buffer solution of potassium biphthalate containing ammonium biffuoride. Foote and Vance (3) employed a buffer solution of acetic acid and ammonium acetate containing sodium fluoride. The purpose of the fluoride in each case was to cut down the activity of the ferric ions so that they would not react with iodide. Crowell and associates (1) have shown that the biphthalate used by Park has no value as a buffer and that the biffuoride is in reality the effective buffer in that method.

Foote and Vance in their procedure introduced the use of thiocyanate toward the end point of the titration. The effect of this addition is to cause the reaction between iodide and cupric ions to go further toward completion and to give end points that are whiter and somewhat sharper than when thiocyanate is omitted. As a result of this behavior the presence of cupric complexes or weakly ionized compounds interferes with the titration less than when thiocyanate is absent. In 21 analyses of cupric sulfide samples containing iron and arsenic in considerable quantities, Foote and Vance obtained an average error of  $-0.05$  per cent and a maximum error of  $-0.11$  per cent. The author of the present paper and associates (1, 2) carried out similar copper sulfide analyses, using biffuoride buffer solutions both with and without thiocyanate, and in both cases obtained practically the same percentage errors as Foote and Vance. It has been their experience that biffuoride buffers give highly satisfactory end points without the use of thiocyanate. However, when analyses are made without thiocyanate the thiosulfate solution should be standardized against copper metal under the same conditions. If thiocyanate is used in the analysis, the thiosulfate may be standardized against iodine or by any accepted iodometric method.

To seek a more satisfactory basis of comparison of the behavior of buffer solutions in order to be able to select those most suitable for the purposes described, the present investigation was undertaken. While the use of thiocyanate tends to extend the choice of satisfactory buffer solutions somewhat, such a study should be not only of theoretical interest but also of practical value in showing that certain buffers have advantages over others in certain cases and what buffers can be used and under what working conditions if the thiocyanate is omitted. The work was confined to solutions which have the proper ionization constants and the salts of which at moderate concentrations do not form objectionable precipitates with cupric ions. The acids selected were acetic, propionic, formic, and hydrofluoric.

In such a study the main reactions to be considered are:



To make the behavior more apparent, Reaction 1 was studied separately by mixing cupric sulfate, potassium iodide, and the buffer solutions in a suitable flask, allowing them to come to equilibrium in a thermostat, and determining the unreduced copper. In order to observe the effects of the various buffer constituents on the iodometric end points, titrations in these buffer solutions with thiosulfate were also made in the usual manner, whereby Reactions 1 and 2 determine the per cent of copper reduced. As a result of this investigation it was hoped to reach conclusions regarding the following points:

1. The effects of pH, concentration of acid, and the salt of the acid on the per cent of copper reduced in fixed initial concentrations of cupric and iodide ions.

2. What solutions can be used and under what conditions in order to work at a pH between 3.2 and 4.0.

3. What solutions are the most suitable in the most general case in which iron is present alone or with arsenic; when arsenic is the only interfering impurity; and when arsenic and iron are absent and the pH may be 3 or less but sufficiently high to cause the oxygen-iodide reaction to be inappreciable.

### Equilibrium Experiments and Iodometric Titrations in Buffer Solutions

**REAGENTS.** In preparing buffer solutions of the acids and their salts, ammonium salts were used in all cases except that of acetic acid, when the sodium salt was employed. Glass apparatus lined with paraffin was used in handling the hydrofluoric acid solutions. The 1.0 *M* hydrofluoric acid buffer solutions consisted of mixtures of the acid and ammonium fluoride, but the 0.10 *M* acid solutions consisted of mixtures of ammonium fluoride and ammonium biffuoride. In the case of biffuoride the "purified grade" was used.

**EXPERIMENTAL PROCEDURES.** In the equilibrium experiments the procedure was as follows: The air in a 200-cc. conical flask was displaced with nitrogen and the following solutions added in the order stated: 25.0 cc. of potassium iodide solution, 50.0 cc. of buffer solution, and 25.00 cc. of 0.1152 *M* copper sulfate. The flask was sealed and rotated in a thermostat at 25° C. until equilibrium was reached. Samples were then removed through a filter and treated with nitric and sulfuric acids. The sulfuric acid solution of cupric sulfate remaining was neutralized with ammonia, acidified with formic acid, treated with iodide, and titrated with thiosulfate.

pH measurements were made by means of the quinhydrone electrode on separate solutions containing the same constituents at the same initial concentrations as those used in the regular runs except that potassium chloride was substituted for the iodide.

In the end-point study, titrations of the iodine in the buffer solutions with thiosulfate were made immediately after adding iodide and copper sulfate. In these experiments the titration during the addition of the last 0.5 cc. took no longer than about 2 minutes.

**RESULTS OF EQUILIBRIUM RUNS.** Results are recorded in Table I and plotted in Figures 1 and 2. Equilibria were established in three types of solutions containing different concentrations of the ammonium or sodium salt of the acids: one in which the ammonium salt alone was used, a second in which the acid concentration was maintained at 1.0 *M*, and a third in which the acid concentration was 0.10 *M*. In Table I are tabulated the percentages of reduced copper and the corresponding pH values. In Figure 1 percentage reduction of the copper is plotted against corresponding salt concentration. In Figure 2 percentage reduction is plotted against pH for the runs in which the acid concentrations are maintained at 1.0 *M* and 0.10 *M*, respectively. In order to observe the effect of salt concentration as well as pH, the numbers corre-



TABLE I. PERCENTAGES OF COPPER REDUCED AND CORRESPONDING PH VALUES IN CERTAIN BUFFER SOLUTIONS

Composition of Equilibrium Solutions		(Initial concentration of copper sulfate = 0.02880 M. Initial concentration of potassium iodide = 0.200 M)										
		Concentration of Salt										
		0.000	0.0500	0.100	0.200	0.400	0.600	0.800	1.00	1.20	1.60	2.00
		Moles per liter										
1.00 M acetic acid and sodium acetate	%	97.9	...	92.4	85.4	70.4	56.5	43.0	30.6	...	...	...
	pH	2.15	...	3.33	3.69	4.01	4.23	4.38	4.50	...	...	...
0.100 M acetic acid and sodium acetate	%	97.3	...	89.6	79.8	61.0	43.9	30.4	19.2	...	...	...
	pH	2.64	...	4.27	4.64	4.94	5.16	5.27	5.37	...	...	...
Ammonium propionate	%	...	...	89.6	76.7	52.3	32.1	18.3	9.5	...	...	...
1.00 M propionic acid and ammonium propionate	%	98.5	96.9	93.8	87.6	73.8	60.2	48.1	35.9	...	...	...
	pH	2.26	3.15	3.46	3.84	4.21	4.39	4.55	4.65	...	...	...
0.100 M propionic acid and ammonium propionate	%	97.8	94.7	90.4	80.9	61.5	47.2	32.9	23.0	...	...	...
	pH	2.72	4.13	4.42	4.76	5.05	5.19	5.33	5.42	...	...	...
Ammonium formate	%	99.5	...	98.0	95.0	89.3	82.4	70.5	55.3	...	...	...
1.00 M formic acid and ammonium formate	%	98.9	...	97.5	95.4	93.3	87.9	83.5	76.1	...	...	...
	pH	1.79	...	2.17	2.57	2.91	3.14	3.31	3.44	...	...	...
0.100 M formic acid and ammonium formate	%	97.4	...	96.5	94.6	90.7	85.6	77.5	63.6	...	...	...
	pH	2.19	...	3.37	3.72	4.09	4.32	4.46	4.79	...	...	...
Ammonium fluoride	%	...	...	...	95.5	91.5	...	73.5	63.0	51.0	19.0	16.6
Ammonium bifluoride	%	...	...	...	98.2	...	...	...	97.3	...	...	96.0
	pH	...	...	2.87	2.84	2.81	...	...	2.72	...	...	...
1.00 M HF and NH <sub>4</sub> F	%	99.5	...	99.3	99.0	98.8	...	98.0	97.3	93.5	85.0	67.0
	pH	1.18	...	1.50	1.72	2.12	...	2.57	2.80	2.95	3.21	3.46
0.100 M HF and NH <sub>4</sub> F	%	...	...	98.5	97.0	94.0	92.4	87.9	83.4	...	...	...
	pH	...	...	2.87	3.28	3.71	3.96	4.16	4.33	...	...	...

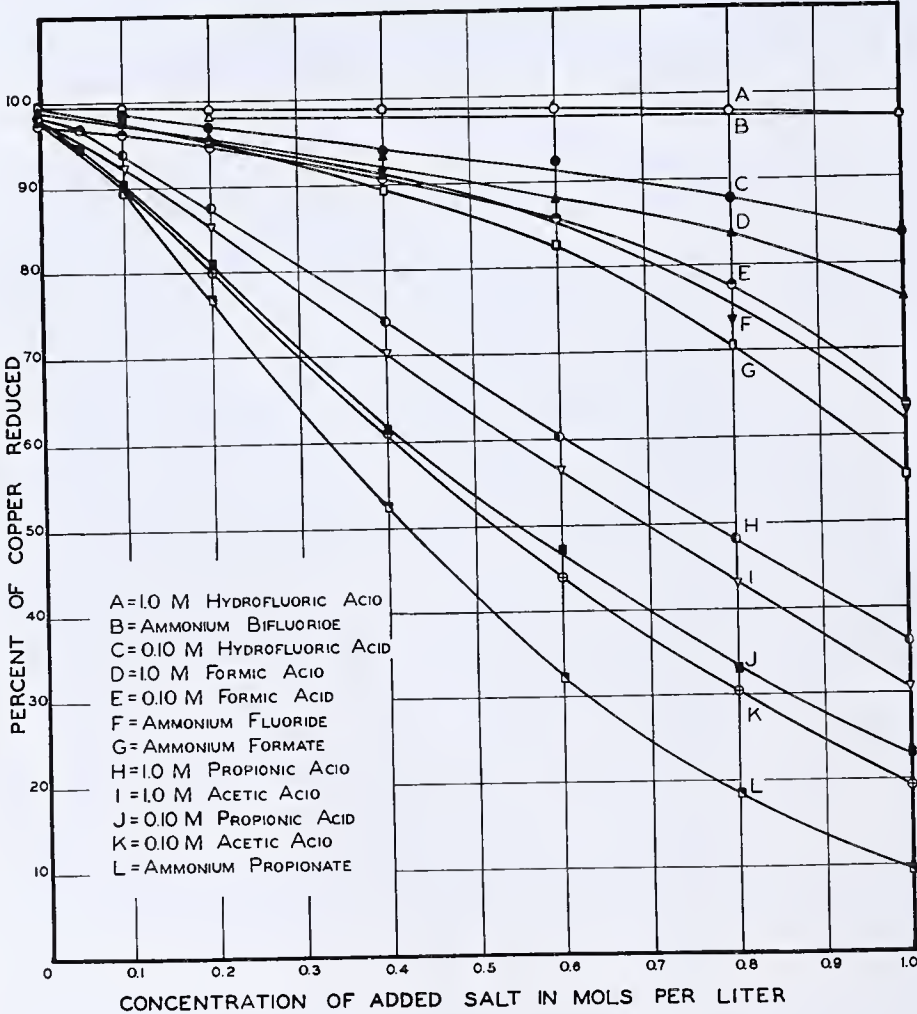


FIGURE 1. RESULTS OF EQUILIBRIUM RUNS

sponding to salt concentration in moles per liter are indicated at the various points plotted:

CONCLUSIONS FROM EQUILIBRIA DATA. A study of Table I and of Figures 1 and 2 considered in conjunction with results of the iodometric titrations of the buffer solutions immediately after the addition of iodide and copper sulfate leads to the following general conclusions:

1. In buffer solutions of propionic, formic, and hydrofluoric acids evidently cupric complexes are formed similar to those in buffer solutions of acetic acid. The lowering of the

per cent reduction of copper at a given initial concentration of cupric ion, iodide, salt, and acid roughly seems to depend upon the ionization constant of the acid. Acetic and propionic acids, whose ionization constant at 25° C. are  $1.8 \times 10^{-5}$  and  $1.4 \times 10^{-4}$  respectively, show the lowest per cent reduction. Formic acid with a constant of  $2.4 \times 10^{-4}$  has the next higher per cent and hydrofluoric acid with a constant of  $6.9 \times 10^{-4}$  has the highest per cent. The last named no doubt has its value raised somewhat by reason of the bifluoride equilibrium.

2. The per cent reduction in buffer solutions of a given acid does not depend so much upon pH as upon actual concentration of acid and of salt, especially of salt. A tenfold change can be made in the hydrogen ion concentration without materially affecting the per cent reduction. At a fixed acid concentration a tenfold increase in salt concentration may lower the reduction 3 to 15 per cent in hydrofluoric acid, 20 to 30 per cent in formic acid, and 60 to 70 per cent in acetic and propionic acids. For a given salt concentration a tenfold increase in acid concentration may raise the percentages 3 to 15 per cent.

3. Results of titrations of iodine in the buffer solutions immediately after the addition of iodide and copper sulfate in general agreed with those obtained with copper sulfate containing no buffer constituents with a few hundredths of a per cent if the equilibrium per cent reduction was no lower than

85 to 90. On this basis satisfactory end points without the use of thiocyanate can be obtained with the various buffers at a pH between 3.2 and 4.0 if, at the concentrations of iodide and cupric ions commonly employed, the concentrations of the salt of the acid are not much greater than the following values: fluoride, 1.0 to 1.6 M; formate, 0.6 to 1.0 M; and acetate and propionate, 0.1 to 0.2 M. If thiocyanate is added, probably these values can be materially increased. From the standpoint of salt effect the superiority of hydrofluoric acid buffers over the others is evident, and formic acid



buffers have an advantage over those of acetic and propionic acids. Since hydrofluoric acid buffers, prepared from ammonium bifluoride, can serve the double purpose of acting as an effective buffer and of forming a complex with ferric ions, there is little doubt of their superiority when iron is present alone or with arsenic. Since hydrofluoric acid solutions because of their effect on glassware probably would not be selected for their buffer action alone, formic acid solutions should show themselves the most satisfactory in iron-free solutions containing arsenic and in iron- and arsenic-free solutions in which it is desired to work at a pH between 2 and 3, a region within which the rate of the oxygen-iodide reaction is inappreciable. As an example of the latter case, this laboratory now employs formic acid instead of acetic in the standardization of thiosulfate solutions with copper metal.

### Determination of Copper in the Presence of Arsenic Using Formic Acid Buffer

Determinations of copper in solutions of copper sulfate and cupric sulfide were made using buffer solutions of formic acid containing 0.2 gram of arsenic. In the case of the solutions the procedure was as follows: To 40 cc. of a solution containing the arsenic and the same amount of copper as was employed in the equilibrium runs was added enough 6 *N* ammonium hydroxide to give the solution a distinctly recognizable odor of ammonia. Sufficient 4 *N* formic acid was then added just to dissolve the precipitate formed and the titration was completed with iodide and thiosulfate. The procedure in the case of cupric sulfide was the same as that de-

scribed for the bifluoride runs (2) except that after the addition of ammonia, instead of adding bifluoride, sufficient 4 *N* formic acid was added just to dissolve the precipitate. The pH of the solutions was determined with quinhydrone before the addition of iodide. Results of seven titrations of copper sulfate solutions without the addition of thiocyanate showed an average error of  $-0.03$  per cent and a maximum error of  $\pm 0.13$  per cent. Results of analyses of seven samples of copper sulfide during which thiocyanate was added showed practically the same percentage errors as the solutions. The percentage errors were determined on the same basis as that used for bifluoride (1). The pH was between 3.5 and 3.7. As in the case of bifluoride buffers, these results indicate that satisfactory determinations can be made in formic acid buffers without thiocyanate.

### Summary

In a study of the reaction between copper sulfate and potassium iodide in buffer solutions of acetic, propionic, formic, and hydrofluoric acids, propionates, formates, and fluorides lower the activity of the cupric ions in much the same manner as acetates. At a given initial concentration of copper and of iodide the lowering of the per cent of copper reduced is not governed so much by pH as by the concentrations of acid and of salt, especially of salt. In the iodometric determination of copper in the presence of iron and arsenic at the concentrations of copper and of iodide commonly used, satisfactory end points in buffer solutions of these acids with a pH between 3.2 and 4.0 can be obtained without the use of thiocyanate if the maximum concentrations of the salt of the acid do not exceed 0.1 to 0.2 *M* for acetic and propionic acids, 0.6 to 0.7 *M* for formic acid, and 1.0 to 1.7 *M* for hydrofluoric acid. In solutions in which iron is present alone or with arsenic, ammonium bifluoride solutions are the most suitable. In iron-free solutions containing arsenic and in solutions free from iron and arsenic in which it is desired to work at a pH between 2 and 3, formic acid has an advantage over acetic and propionic acids. Results obtained without the use of thiocyanate in formic acid buffer solutions containing arsenic but free from iron showed practically the same accuracy and precision as those obtained with the addition of thiocyanate, and also those obtained in a previous work in which buffer solutions of bifluoride were employed with and without the addition of thiocyanate. If thiocyanate is not used in the analysis, the thiosulfate solution should be standardized with copper metal under the same conditions.

### Acknowledgment

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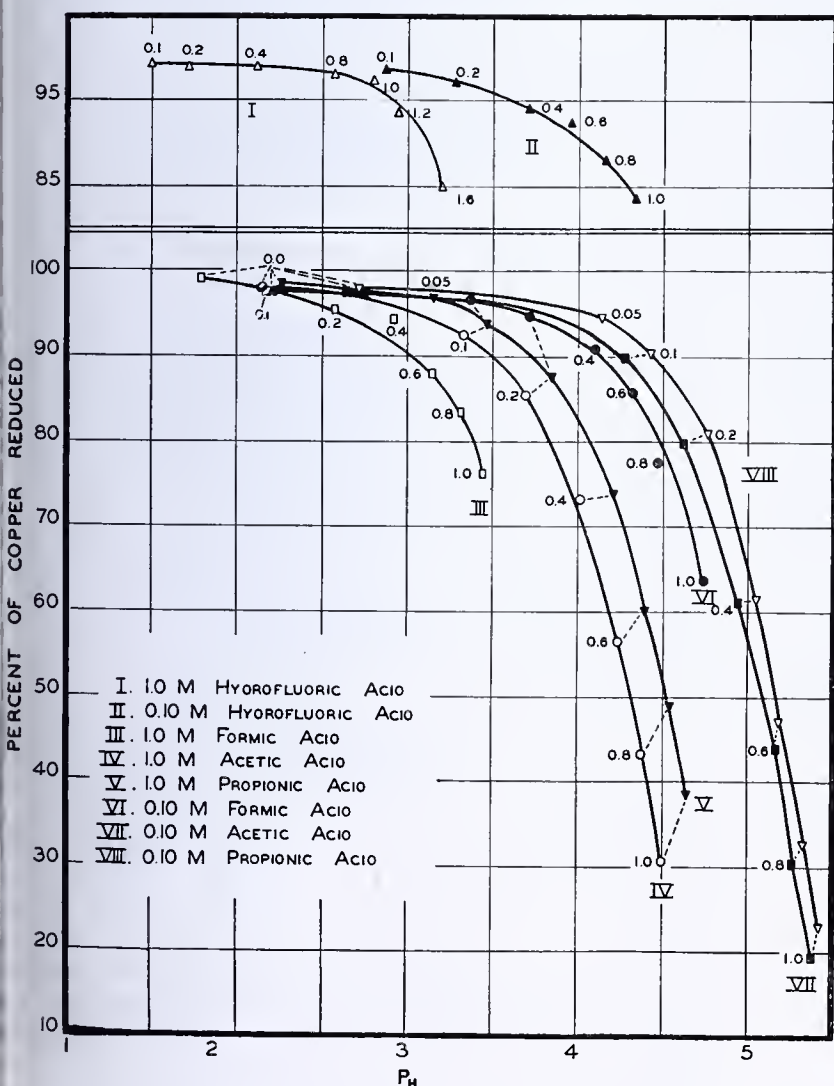


FIGURE 2. RESULTS OF EQUILIBRIUM RUNS



# Recovery of Platinum Used in the Determination of Potash

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MANY reports have been made on the recovery of the platinum used in the Lindo-Gladding method for the analysis of potassium. Almost all of these direct the use of one of three reducing agents—i. e., hydrogen generated by a metal and hydrochloric acid (4, 8), a boiling solution of sodium formate (1, 7), or a boiling solution of ethyl alcohol (5, 6). The first two methods introduce chemicals that will not volatilize at water-bath temperatures and may adhere to the platinum during the reduction process. The reduction with alcohol is slow and is said (6) to be due to the aldehyde content.

In a recent article (2), results of a questionnaire were reported which indicate that about 80 per cent of the analytical chemists are using zinc or aluminum in acid solution for the reduction of the chloroplatinates. The same report shows that 50 per cent are in doubt as to the purity of the recovered platinum. Because of dissatisfaction with recorded methods for this reduction, the authors have worked out a simple procedure that requires less attention, recovers almost 100 per cent of the platinum used, and produces a pure chloroplatinic acid.

## Procedure

From the alcoholic wash solution obtained in the Lindo-Gladding procedure for potash determination, precipitate the chloroplatinic acid with excess ammonium chloride, using the method suggested by Haigh and Hall (4).

Into a 3-liter wide-mouthed bottle, introduce approximately 2000 cc. of distilled water and 25 cc. of 85 per cent formic acid. As the potassium determinations are completed, transfer the potassium and the ammonium chloroplatinates to the bottle, stopper loosely to keep out dust, and allow the mixture to stand at room temperature.

When it becomes necessary to prepare the chloroplatinic acid, decant off the colorless solution, and wash the residue with hot water until free from chlorides. Prepare the chloroplatinic acid in the usual way, by dissolving the platinum in nitrohydrochloric acid, removing the excess of the solvent on the boiling water bath, and diluting the pure chloroplatinic acid to a solution containing 10 per cent of platinum.

## Discussion of the Method

The bottle for the reduction should be one with a wide mouth and sloping shoulders, so that the platinum can be easily removed.

If the asbestos in the Gooch crucible has been treated with aqua regia, all or any part of it may be transferred to the bottle along with the salt. In fact, this addition is advantageous, since the first platinum reduced settles on the asbestos in a finely divided form and, acting as a catalyst, hastens the reduction process.

It is unnecessary to dissolve the salts as they are added. Twenty-five cubic centimeters of the 85 per cent formic acid will reduce approximately 25 grams of the chloroplatinates at room temperature. After this amount of the salt has been added to the bottle, a new solution should be made. Although sodium formate (1, 7) and buffered sodium formate (3) solutions have been used, the addition of an alkali is unnecessary for the reduction by formic acid, either in a cold or in a hot solution. In a cold solution, reduction of these salts will continue to pH 0.9.

Formic acid will reduce a saturated solution of the chloroplatinates in a few minutes at 100° C., but it requires from 3

to 5 days at room temperature. The form in which the platinum is deposited depends upon the temperature to which the solution is subjected. At high temperatures, sootlike platinum is deposited which adheres to the sides of the container. The reduction may be carried out at this temperature, for although a small amount of carbon always appears, it can be removed with the asbestos by filtration. From 23° to 40° C. metallic scales are produced which do not adhere to the sides of a clean container.

Since the platinum is not to be weighed, it is unnecessary to wash it with alcohol and, in fact, it is undesirable to do so. Reduced platinum in the presence of alcohol and exposed to air, such as in a Gooch crucible under suction, deflagrates with the production of finely divided carbon. This carbon is difficult to remove, and is one of the causes of the dark-colored impure chloroplatinic acid so often obtained.

After the reduced platinum and the asbestos have been washed free of impurities, they are transferred, without drying, to an evaporating dish. When the platinum has completely dissolved in the aqua regia, it is advantageous to allow the solution to stand overnight. Any sediment settles out and is filtered off along with the asbestos. The solution is then freed of nitric and hydrochloric acids in the usual way.

The authors have found three satisfactory methods for making the calculations to obtain a chloroplatinic acid solution containing 10 per cent of platinum.

TABLE I. SPECIFIC GRAVITY OF CHLOROPLATINIC ACID CONTAINING 10 PER CENT OF PLATINUM

Sample number	I	II	III
Weight of platinum ignited to 1100° C.	5.5913	7.5105	4.7417
Dilution of H <sub>2</sub> PtCl <sub>6</sub> , cc.	55.90	75.10	47.40
Sp. gr. at 25° C. of diluted H <sub>2</sub> PtCl <sub>6</sub> (containing 10% of platinum)	1.1553	1.1552	1.1551

As shown by Table I, the specific gravity of the required solution should be 1.1552 at 25° C. If the solution were diluted to 1.1550 specific gravity, it would contain 9.98 per cent of platinum; or to 1.1560, it would contain 10.05 per cent of platinum. Using the specific gravity of a more concentrated solution, calculations for the dilution may be made by alligation. This method requires the least time and work because it is unnecessary to dry and weigh the reduced platinum; moreover, it is just as accurate as calculating the dilution from the weight of pure platinum. Care must be taken however, to remove all the hydrochloric acid before the specific gravity is determined.

TABLE II. ERROR IN CHLOROPLATINIC ACID IF PLATINUM IS DRIED AT 130° C.

Sample number	I	II	III
Weight of platinum			
A. Dried at 130° C.	5.6501	7.6005	6.547
B. Ignited at 1100° C.	5.5913	7.5105	6.472
Platinum in H <sub>2</sub> PtCl <sub>6</sub> solution, %			
Calculated from A	9.89	9.88	9.88
Calculated from B	10.00	10.00	10.00

If calculations for making the chloroplatinic acid solution are to be made from the weight of the reduced platinum, it is unnecessary to dry the platinum at a temperature above 130° C.

As shown in Table II, the chloroplatinic acid solution calculated from the weight of the platinum dried at 130° C. would



contain slightly less than the usual 10 per cent of platinum. Since an excess of chloroplatinic acid, sufficient to compensate for this difference, is always used for precipitation of the potassium chloroplatinate, this slight error is negligible.

Dilution of the chloroplatinic acid may be made from the weight of the recovered chloroplatinic acid crystals. Because of the variable amounts of water of crystallization and the hygroscopic nature of chloroplatinic acid, this method is the least satisfactory. Usually, the solution will contain from 8.8 to 10.2 per cent of platinum.

Since the chloroplatinic acid need not contain exactly 10 per cent of platinum, any of these methods will produce the desired solution sufficiently accurately for all practical purposes.

### Summary

The prevalent methods for the recovery of chloroplatinic acid from the chloroplatinates obtained in the Lindo-Gladding procedure for the analysis of potassium require much attention and frequently give an impure product. The use of formic acid at room temperature for the reducing agent saves much effort and gives a platinum from which pure chloroplatinic acid is always recovered. Except for the addition of the chloroplatinates as they are obtained, this reduction process requires no attention after the formic acid solution is prepared.

The chloroplatinic acid solution containing 10 per cent of platinum can be made most efficiently and accurately by diluting the recovered chloroplatinic acid to a solution having the specific gravity of 1.1552 at 25° C.

Unless the platinum is to be ignited sufficiently to oxidize all the carbon present, it should not be washed with alcohol and dried by suction. With this treatment the platinum often deflagrates, finely divided carbon is produced, and a dark-colored impure chloroplatinic acid results.

Formic acid reduction, at room temperature, yields a platinum which does not adhere to the sides of a clean container. Unless the longer time required for the reduction is a deterring factor, this process is suitable for those analyses in which the potassium is calculated from the weight of the platinum reduced from the potassium chloroplatinate.

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## Ash Determination in Cereal and Other Vegetable Materials

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THE author has used for some time a very satisfactory method for ash determination in cereal products.

The determination of ash in such materials as wheat flour is ordinarily a long and often unsatisfactory procedure. If the combustion takes place in an electric or gas muffle at low heat, often 12 hours or more are necessary. At higher temperatures, fusion of the ash, especially of the ash of spring wheat flours, causes occasional occlusion of carbon which can be oxidized only with great difficulty at high heat. The ash of wheat flour is acid in reaction and consists mainly of acid phosphates of potassium, etc. Many methods have been proposed, using added calcium salt solutions, but the hygroscopic character of the calcium compounds and their absorption of carbon dioxide have caused difficulties by the increase in weight which takes place even when the ash is promptly weighed. Organic salts of magnesium added in the form of solutions have been proposed, but in some cases the solutions have been spoiled by mold growths, and with water solutions considerable time is lost by the necessity of drying before beginning the combustion. Working and Anderson (1) proposed the use of a 70 per cent alcoholic solution of magnesium nitrate. Independently the author found that magnesium nitrate was the best of the magnesium salts, that it is not subject to mold growth, its oxygen content helps the oxidation of the flour, and it contributes no carbon to the combustion.

After considering a number of solvents, carbitol (monohydric ether of diethylene glycol) was adopted. It has a moderately high boiling point, a low vapor pressure, good solvent action on magnesium nitrate, low viscosity, and very rapid penetrating or wetting power for even the finest milled flours; it burns away quickly without sputtering and, in the proportions suggested, leaves a light, fluffy, nonhygroscopic, white ash. It may be added to the flour from a pipet or by some other

appliance capable of dispensing small amounts accurately. The 2-ml. dispensing pipet holding 1 liter, made by the Scientific Glass Apparatus Company, Bloomfield, N. J., has been found very accurate and useful. The apparatus preserves the solution without loss or concentration by evaporation of the solvent and consequent inaccuracy.

Following this method 6.358 grams of magnesium nitrate,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , are weighed into a 1-liter measuring flask. The nitrate is dissolved in carbitol by shaking and finally made up to the mark. For patent and straight grade flours, exactly 2 grams are weighed out in a weighed porcelain, silica, or platinum crucible or ignition capsule of approximately 8-ml. capacity, and 2 ml. of the solution are added to the flour. For clear flours, 1 gram of flour is used; for lower grades, 0.75 gram. The solution is added to the crucible, allowing about 0.25 minute for the solution to drain, then the tip of the dispenser is touched to the inner edge of the crucible. The crucible is placed over a Meker or Fisher burner and the gas ignited for about 10 seconds or until the contents of the crucible begin to burn. The gas is then turned off and the carbitol allowed to burn away quietly. After the flame has flickered out, the burner is again lit and the flour allowed to burn, or it may be placed in the muffle for 1 to 2 hours at bright orange heat. It yields a white or faintly grayish ash.

Before using a new lot of the nitrate solution, the yield of magnesium oxide is determined by weighing an empty crucible, adding 2 ml. of solution, allowing the carbitol to burn off, then strongly igniting until the residue is white. After cooling, the crucible is weighed. The weight of magnesium oxide obtained (which is calculated for 2 mg.) is subtracted from each determination.

Duplicates agree accurately with each other and in comparisons with flours ashed without addition of solution, the results usually check within 0.002 per cent.

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# Mineral Oil Deterioration

## A Revised Grignard Apparatus

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THE continued use of a Grignard reagent (methyl magnesium iodide) in the study of mineral oil deterioration has led to the refinement of the apparatus. In conjunction with the revision of the apparatus, various tests have been carried out to obtain quantitative determinations with the Grignard reagent of ketones, esters, and peroxides such as may be found in petroleum oils.

For the past few years the Grignard apparatus as described by Larsen (2, 4) has been used in these laboratories as an analytical tool in the study of mineral oil deterioration. The results obtained were very promising, and have justified the improvement of the apparatus and procedure so as to give more consistent and accurate results, and to increase the speed and ease of manipulation.

### Apparatus

The following description explains Figure 1. The Grignard reagent (methyl magnesium iodide) is introduced through the female joint and stopcock at the top of reservoir *C* (capacity 500 cc.). One filling is enough for at least 300 determinations. The greaseless stopcock, *D*, consists of a glass rod (5 mm.), one

end of which is tapered and ground, and which fits into a ground-glass aperture with re-enforced walls. The other end is sealed by means of about 4 cm. of pressure tubing (whose inner walls were previously wet with castor oil) which is wired to the tube and rod, a type of seal which gave no leakage trouble. The Grignard reagent can thus be easily transferred from reservoir *C* to buret *F* by manipulation of this joint. *E* is a greaseless stopcock similar to *D* except that the glass rod is 8 mm. in diameter. The 2-cc. reagent buret, *F*, graduated to 0.02 cc., was calibrated while the rod was in it. Reservoir *C*, joint *D*, and the top of buret *F* are covered with black cloth to protect the reagent from light. The reaction flask, *G*, has a volume of about 70 cc., is stirred by the method previously described (4), and simply slides on and off of the male joint, *H*. The gas buret, *J*, is a 25-cc. buret graduated to 0.05 cc. In order to take care of the gas expansion upon heating, a reservoir was provided at the bottom of the buret. The purifying train consists of a heated tube containing copper gauze, followed by tubes of Dehydrite, phosphorus pentoxide, and Ascarite as previously described (4).

### Procedure

Flask *G* is cleaned after use by washing with successive portions of benzene, acetone, dilute hydrochloric acid, distilled water, and methanol. Ether was not used as a final solvent because it was found that slight traces of ether vapor rapidly dissolve in the isoamyl ether of the Grignard reagent, creating a reduced pressure. The flask is dried by gentle heating with a Bunsen flame while blowing in a slow current of dry nitrogen by means of a glass tube which projects to the bottom of the flask. After the flask is dry, the flame is withdrawn, and nitrogen is allowed to flush the flask for about 15 minutes. All apparatus, such as reaction flasks and pipets, are kept in a hot-air oven when not in use. To save time it is advisable to have two reaction flasks. The oil buret, *I*, and male joint, *H*, are cleaned similarly by placing rubber tubing at the mouth of the buret and drawing up through joint *H* successive portions of the same cleaning solvent used above.

Stopcock *M* is then opened, and a Bunsen flame is gently waved over joint *H* and buret *I* as nitrogen is sweeping out through them. Nitrogen is allowed to flush through for about 1 minute. Joint *H* is now greased and the dry flask, *G*, attached to it. This joint is a drip joint and extends far enough down into the female part so that there is no chance of the reagent touching the grease. The stopcock at the base of buret *I* is then closed, and stopcock *K* at the top of the gas buret is adjusted so that nitrogen flows through the groove in the stopcock and out into the atmosphere. Nitrogen is allowed to pass through for 5 minutes, after which stopcock *K* is adjusted so that the buret is connected to the system, and stopcock *M* is closed.

The system is tested for leaks by lowering the leveling bulb and observing whether the reading remains constant for at least 5 minutes. A beaker of water whose temperature is determined to a tenth of a degree is brought up under flask *G*, and after 5 minutes the reading on buret *J* is taken. Stopcock *L* is opened and then closed to allow a few cubic centimeters of nitrogen to flow into the reservoir, and leveling bulb *N* is lowered slightly so as to create a reduced pressure. The reading on buret *F* is taken, and stopcock *E* is opened slightly to allow 1 cc. of reagent to drop into reaction flask *G*. Five minutes are allowed for the system to come to equilibrium, after which a reading is taken on buret *J*. The initial displacement is always larger than the volume of reagent added. This so-called blank reading

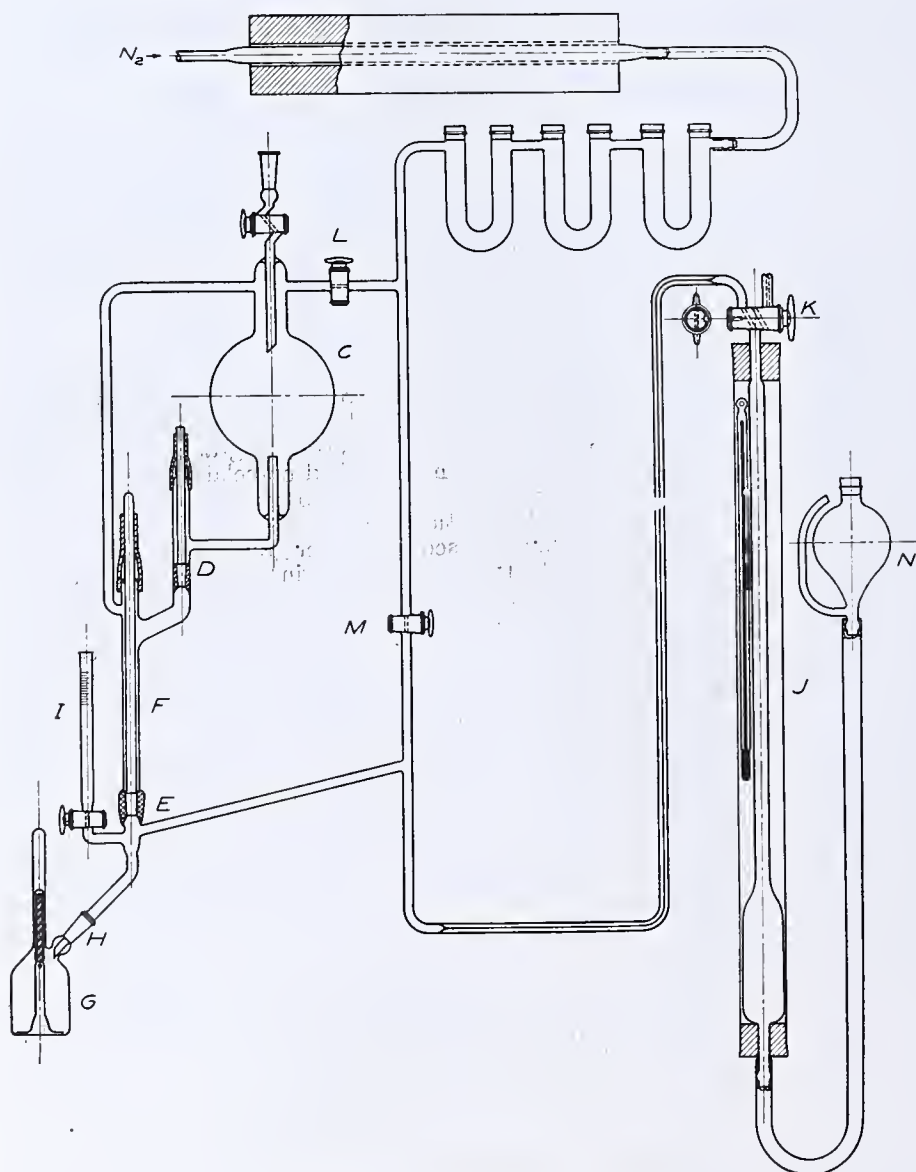


FIGURE 1. GRIGNARD APPARATUS



not always constant, and ranges from 0.20 to 0.80 cc., depending on how dry the system is.

A suitable and weighed amount (4 to 8 cc.) of oil is now transferred from the weighing vessel to buret *I* (in small portions, since *I* holds only 4 cc.). The oil is introduced slowly into reaction flask *G* so that no appreciable afterdrainage results. The solenoid stirrer is started, and thereafter the procedure is the same as that previously described (4) except that 4 cc. of aniline are added instead of water, and the temperature of the water surrounding flask *G* is taken to a tenth of a degree upon each reading of the gas buret.

After the volume readings of methane evolved at room temperature have been obtained, a temperature correction is applied by the use of the following formula which also brings the volumes of methane evolved to normal temperature and pressure conditions:

$$V_0 = \frac{273}{760} \left[ \frac{P}{T_B} (V_2 - V_1) + PV_e \left( \frac{T_{e1} - T_{e2}}{T_{e1}T_{e2}} \right) \right]$$

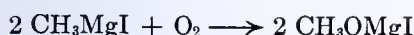
where  $P$  = atmospheric pressure  
 $T_B$  = gas buret temperature  
 $V_2$  = final reading on gas buret  
 $V_1$  = initial reading on gas buret  
 $V_e$  = approximate volume of system  
 $T_{e1}$  = initial temperature of water surrounding reaction flask  
 $T_{e2}$  = final temperature of water surrounding reaction flask

The results obtained are expressed as cubic centimeters of methane (at normal temperature and pressure) evolved per kilogram of oil, but may be transferred into other equivalents such as cubic centimeters of oxygen per kilogram.

Aniline was substituted for water in the standardization of the Grignard reagent after investigation of the error caused by the high vapor pressure of water at room temperature. Standardization with water (using a drying tube as described by Larsen, 4) gave a value of 13.5 cc. of methane evolved per cubic centimeter of Grignard reagent, while with aniline the value obtained was 9.2 cc. Experiments made by adding water to the clean and dry system showed that errors of this order of magnitude were caused by the vapor pressure of water, and not by incomplete reaction with aniline. Check standardizations yielded 9.40, 9.10, and 9.16 cc., the maximum deviation from the mean being less than 2 per cent.

## Results

**OXYGEN.** It is well established that oxygen reacts with Grignard reagents:



Experiments with gaseous oxygen and methyl magnesium iodide indicate that the reaction is rapid and complete. In oxidized oils, therefore, the Grignard reagent reacts not only with the oxygenated compounds but also with dissolved oxygen. The data on the measurement of dissolved oxygen in oils by the Grignard reagent are not yet complete, but the higher Grignard "added" values (1) of oils saturated with oxygen as compared to those saturated with pure nitrogen indicate that the reagent and the dissolved gas do react.

**KETONES.** Quantitative measurements of benzophenone by the Grignard reagent have been made by Kohler and his co-workers (3). In order to test the accuracy of the apparatus, a solution of known concentration of benzophenone in xylene (distilled over sodium wire) was treated with the Grignard reagent. The results obtained (1.04 moles of methyl magnesium iodide consumed per mole of benzophenone) attest to the effectiveness of the apparatus.

**ESTERS.** A known solution of phenyl benzoate in dry xylene, upon which a blank test had been made, was prepared and treated with the Grignard reagent. The results obtained (1.92 moles of methyl magnesium iodide consumed per mole of phenyl benzoate, with no methane evolved) gave good evidence of the sensitivity and accuracy of the methyl magnesium iodide with esters of this type.

However, it was desirable to test the sensitivity of the Grignard reagent with the esters of high molecular weight such as may be formed in oils. Therefore "ester gum," preponderantly a triglyceryl ester of abietic acid (formula  $\text{C}_{63}\text{H}_{92}\text{O}_6$ ), was dissolved in standardized xylene and treated with methyl magnesium iodide. The amount of free abietic acid in the sample was obtained by potentiometric titration. The results obtained are listed below:

Run	Moles of $\text{CH}_3\text{MgI}$ Evolved	per Mole of $\text{CH}_3\text{MgI}$ Added	Mole of Ester Consumed
1	3.5	2.3	5.8
2	4.0	1.8	5.8
3	3.5	2.8	6.3
4	4.0	2.7	6.7
Av.	3.7	2.4	6.1

The theoretical amount of Grignard consumed is 6.0 moles. Whether the methane evolved is due to splitting of the ester and subsequent enolization to give an active hydrogen is open to conjecture. At any rate, the significant fact is that the "Grignard consumed" value gives a measure of the ester content (3). However, more determinations with such high molecular weight esters (and in a purer state) must be made before any definite conclusions are drawn.

**PEROXIDES.** During the study of the oxidation of decalin, a crystalline peroxide was formed. The decalin was heated in an air-oven at 90° to 100° C. while oxygen was bubbled in through a sintered-glass disk for approximately 46 hours. The decalin was then vacuum-distilled until a straw-colored, rather viscous liquid remained which, upon cooling, gave a mush of needlelike crystals. Upon filtration and recrystallization from ligroin, long white needles of a melting point 94–5° C. were obtained. Assuming the peroxide to be 1 molecule of decalin plus 1 molecule of oxygen ( $\text{C}_{10}\text{H}_{18}\text{O}_2$ ), its theoretical percentage composition is 70.5 per cent carbon and 10.62 per cent hydrogen. A carbon-hydrogen analysis substantiated this assumption, values of 69.8 per cent carbon and 10.4 per cent hydrogen being obtained.

A weighed amount of the peroxide was then dissolved in anhydrous xylene and treated with the Grignard reagent. Methane was evolved, indicating an active hydrogen. Since the structure of decalin peroxide is more or less in dispute, it seemed natural to postulate that this peroxide is of the  $\text{R}-\text{O}-\text{O}-\text{H}$  type. Assuming this to be true, one mole of peroxide would react with 2 moles of methyl magnesium iodide (one of them evolving methane). A comparison of the theoretical vs. experimental values based upon this assumption was favorable:

1. 0.96 mole of  $\text{CH}_3\text{MgI}$  evolved per mole of decalin peroxide
2. 1.07 moles of  $\text{CH}_3\text{MgI}$  added per mole of decalin peroxide

The Grignard reagent apparently reacts quantitatively with this type of peroxide.

TABLE I. SUMMARY OF RESULTS

Compound	Moles of $\text{CH}_3\text{MgI}$ Evolved	per Mole of $\text{CH}_3\text{MgI}$ Added	Mole of Compound Consumed	Theoretical (1)
Benzophenone	None	1.04	1.04	1.00
Phenyl benzoate	None	1.92	1.92	2.00
"Ester gum"	3.7	2.4	6.1	6.0
Decalin peroxide	0.96	1.07	2.03	2.00

## Summary

A compilation of the results obtained, given in Table I, shows the accuracy of the quantitative determination, by the Grignard reagent, of the types of compounds—ketones, esters, and peroxides—which one may expect to find in oxidized petroleum oils.



### Acknowledgment

The development of the application of the Grignard reagent to mineral oil deterioration is part of a joint research project of the Massachusetts Institute of Technology and the Utilities Co-ordinated Research, Inc. (Association of Edison Illuminating Companies), on electrical and chemical studies of insulating oil deterioration. The authors wish to acknowledge the cooperation of the Committee on Insulating Oils and Cable Saturants, U. C. R., Inc., Herman Halperin, chairman, and other committees representing the oil-refining and electrical manufacturing companies.

The authors also wish to express their indebtedness and appreciation to J. C. Balsbaugh and J. L. Oncley for their interest and cooperation.

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## Improved Gas Analysis Apparatus

### Employing a Simplified Automatic Absorption Pipet

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IN THE past few years attention has been directed toward the design of gas-absorption pipets by which the rate of absorption of gases in liquid reagents may be increased. Egerton and Pidgeon (2) described a device whereby the absorbing reagent was sprayed through the gas in the form of a fountain. This was effected by forcing the reagent through a constriction in the pipet by manually raising and lowering a reservoir of mercury connected to the pipet. An improved modification was devised by Egerton and Smith (3) but the fountain was still effected by manual operation. Later, Weydanz (7) published a description of a pipet in which a portion of reagent was trapped in a specially designed cup as the sample was introduced into the pipet. This liquid then dripped through the gas from capillary holes in the cup. The glass blowing of the pipet was involved and little saving in time was gained.

The first automatic pipets were developed and in some forms patented by Huff (4). In these forms a continually fresh surface of absorbent in contact with the gas was secured by the motion, inside the pipet, of a glass-covered iron piston actuated by an outside electromagnet. Later another mechanized gas analysis apparatus was devised by Kleiber (5) and modified by Winchester (8, 9). The complexity of this apparatus precludes its general use in gas analysis.

In the Huff electromagnetic pipets the rate of agitation is determined by the time required for the piston to fall (or rise) by gravity through the reagent. Consequently, a single standard pipet will not give optimum results with all reagents, and it is necessary to have pipets of slightly different design for the use of reagents of markedly different viscosities and specific gravities. The loose piston makes it necessary to exercise extreme care in changing solutions and in cleaning the pipets to avoid breakage. These difficulties are overcome by a pipet that is designed in the same general manner as the Huff pipet and utilizes alternating air pressure as the pumping mechanism in a way which is analogous to that described by Huff in his original patent application dated July 22, 1931. This design was not patented by Huff and does not appear to have been published elsewhere.

### Apparatus

The details and dimensions of the pipet are given in Figure 1. The pipet occupies approximately the same space and can be

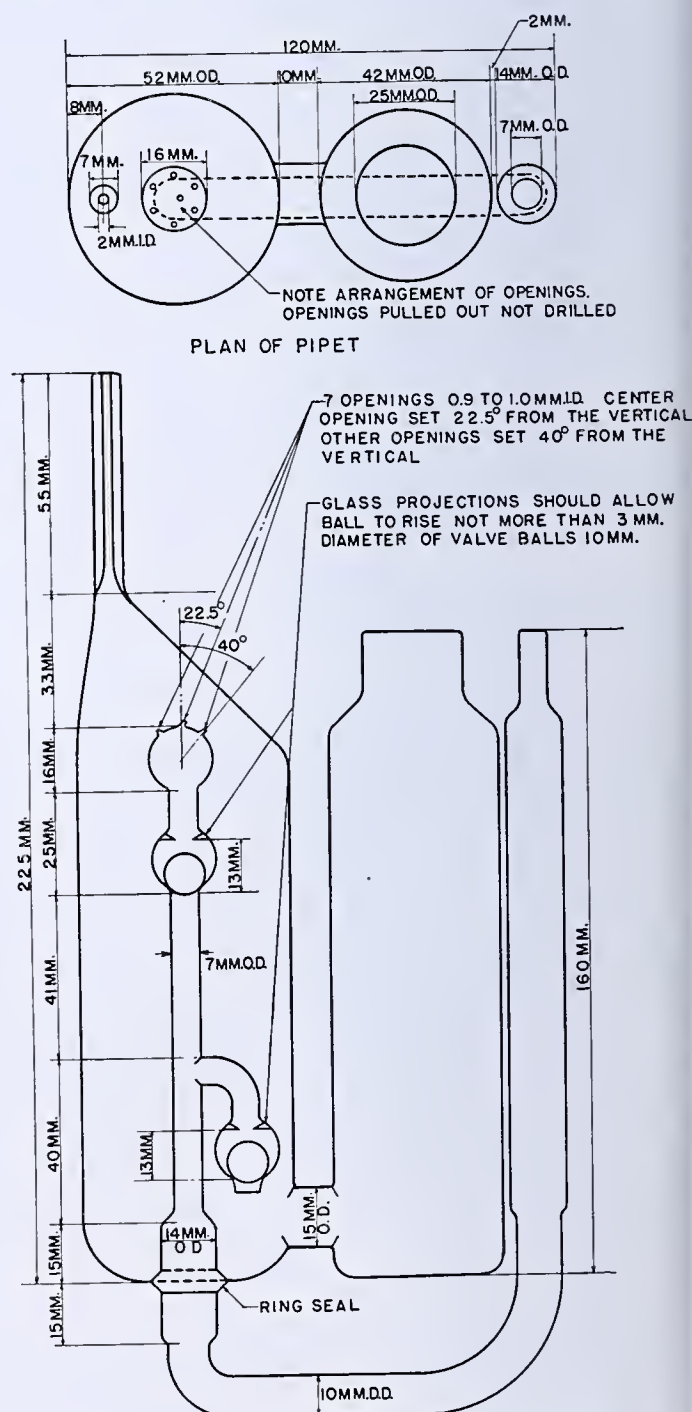


FIGURE 1. PLAN AND ELEVATION OF PIPET



supported in the same manner as the conventional bubbling and rod filled pipets with the exception of the space needed for the spray-head supply tube (compare *H*, Figure 3) which requires a supporting member somewhat longer than the usual commercial one. Three pieces of accessory equipment (Figure 2) are essential: a U-tube, *E*, partly filled with mercury; a three-way stop-cock, *C*; and a push-pull air pump, *A*, and motor drive, *B*.

As shown in Figure 3, the mercury seal functions as a simple U-tube, although it is constructed with two concentric tubes since that form is stronger and more compact. The volume of each arm of the mercury seal is the minimum size that will effect the transmission of the impulse to the pipet without appreciable damping. Since a satisfactory control cock was not readily available, the air cock, *C*, was made from a Lunkenheimer brass drain cock [The Lunkenheimer Co., Cincinnati, Ohio, Catalog No. 58 (Condensed Edition) March 1933; Figure 981, one-eighth inch brass drain cock] (6).

A mercury seal and an air cock for each pipet were placed on a panel that was fastened conveniently on the front of an Orsat apparatus. The push-pull air pump, *A*, was made from an F. C. Spark Plug Co. diaphragm fuel pump (for mounting on V-8 motors) by removing the valves and strainers, plugging the inlet port, and loading the diaphragm with suitable spring tension.

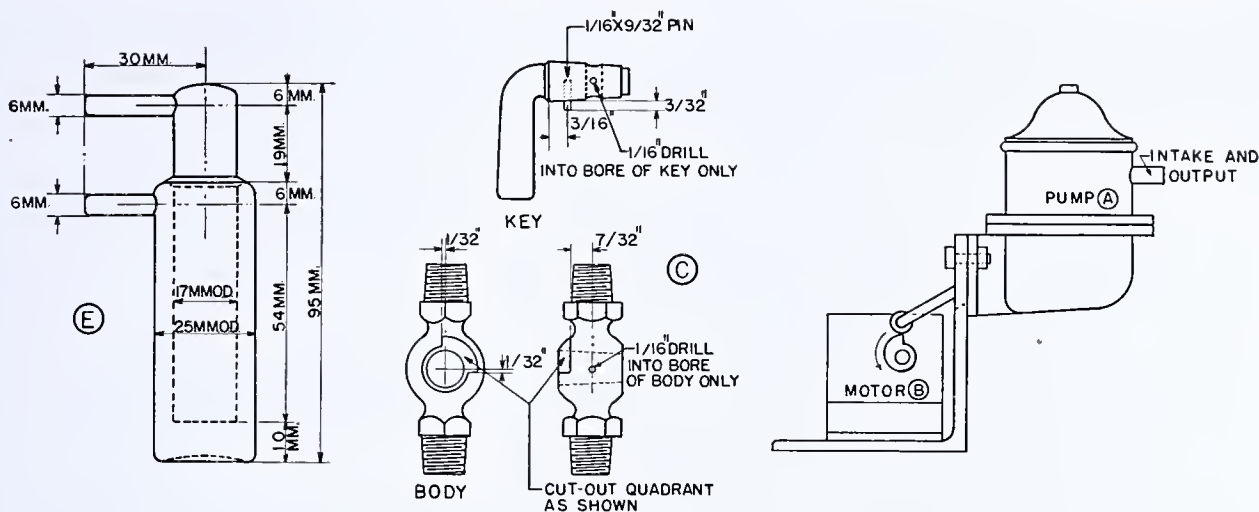


FIGURE 2. ACCESSORY EQUIPMENT

- |                |                 |
|----------------|-----------------|
| A. Air pump    | C. Air cock     |
| B. Motor drive | E. Mercury seal |

A roller on the end of the rocker arm of the fuel pump was actuated by a cam operated at 180 revolutions per minute by means of a small electric motor and gear train, *B*. There is, however, no critical value for the speed.

The pump system is shown diagrammatically in Figure 3. The diaphragm air pump, *A*, is actuated by the motor, *B*. The air cock, *C*, is shown in the operating position. The off position is reached by turning the cock 90° clockwise. This closes the line to the air pump, making it available for use with another pipet, and at the same time vents the mercury seal, *E*, to the atmosphere at opening *D*, thus causing the liquid in the spray-head supply tube, *H*, to return to its original level. The mercury seal also protects the metal parts of the apparatus from fumes given off by absorbing liquids such as fuming sulfuric acid and shields reagents such as alkaline pyrogallol from the air. In operation the impulses from the diaphragm pump are transmitted by the mercury seal to the spray-head supply tube where the absorbing liquid is alternately pushed down and pulled up. As the liquid is pushed down, the upper check valve opens, allowing liquid to spray through the gas from spray head *G*. When the liquid is

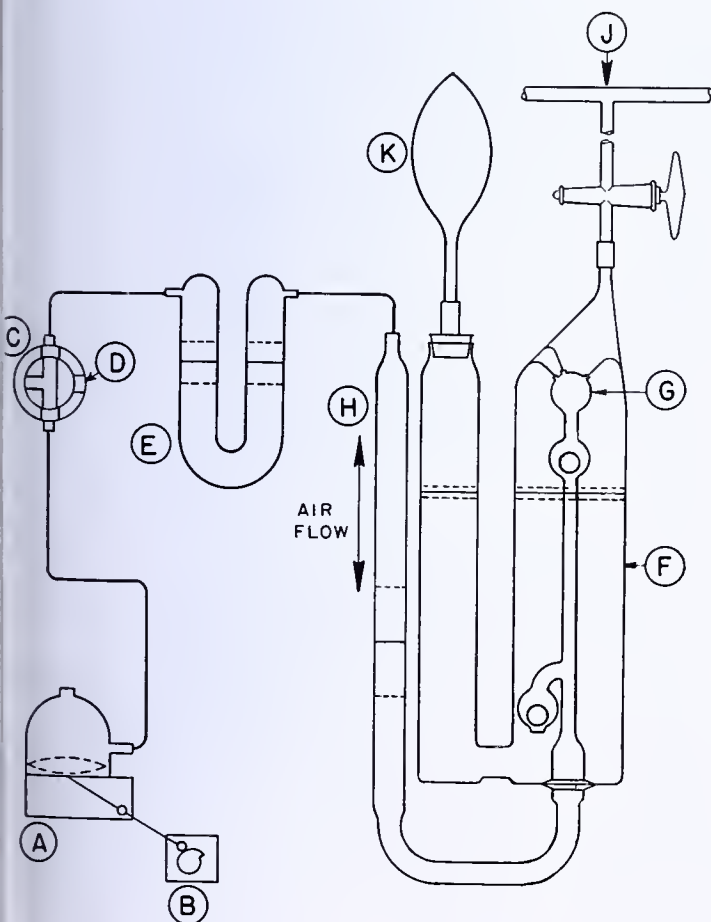


FIGURE 3. DIAGRAM OF APPARATUS

- |                                 |                           |
|---------------------------------|---------------------------|
| A. Diaphragm push-pull air pump | F. Automatic pipet        |
| B. Motor drive                  | G. Spray head             |
| C. Air cock, operating position | H. Spray-head supply tube |
| D. Vent to atmosphere           | J. Orsat manifold         |
| E. Mercury seal                 | K. Rubber Orsat bulb      |

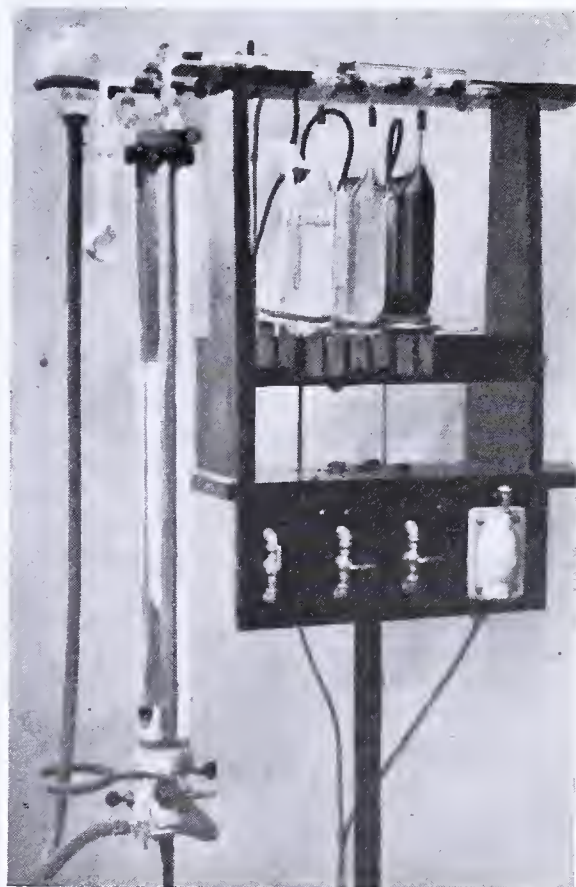


FIGURE 4. GAS ANALYSIS APPARATUS



pulled up, the lower check valve opens, allowing fresh absorbent to flow into the spray-head supply tube.

Figure 4 shows the usual Orsat gas analysis apparatus with the substitution of three automatic pipets for the conventional pipets and the addition of a push-pull air pump and a control panel which supports the mercury seals, air cocks, and a pump motor switch.

### Operation

The performance of an analysis with the apparatus employing the simplified automatic pipet follows the same procedure as that employed with other automatic pipets and differs from that used with the older types of apparatus in that instead of the tedious, exacting operation of running the sample into the pipet and drawing it back into the buret several times, the sample is transferred to a pipet in which it remains until absorption is complete. The absorbent is pumped through and around the gas for a predetermined length of time. During this time no watching is necessary in comparison to the ever-alert attention required with the older method to check and reverse the flow in order to avoid sending the buret confining liquid into the pipet or drawing the absorbent into the buret. While the pumping proceeds other work can be done or another gas analysis apparatus can be operated.

The rate of absorption in the simplified automatic pipet is rapid. The oxygen in 100 cc. of air can be removed so completely in 2 minutes, using alkaline pyrogallol as the absorb-

ent, that it is unnecessary to check the reading. Because of the increased speed of absorption and also because no attention is required during absorption, reagents which heretofore have been too slow-acting for practicable use can be employed (1).

The dependability of the apparatus may be attested to by the fact that equipment is now in use with which more than 10,000 analyses have been performed. The original pump and most of the original pipets are still in use.

### Acknowledgment

The authors are indebted to E. I. Thomas for the design and construction of the air pump.

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## Use of Silica Cotton in Filter Crucibles

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IN SOME recent work on the determination of lead as sulfate it was found that silica cotton (obtained from the Owens-Illinois Glass Company, Toledo, Ohio) is an ideal material for the filtering mats in Gooch crucibles. The lead sulfate precipitate is readily retained by the silica cotton, is easily and quickly washed, and upon ignition at 600° C. no change occurs in the silica cotton. Glass cottons sinter and become friable at this ignition temperature, whereas silica cotton does not sinter below 800° C.

Observations were also made upon the relative merits of silica cotton, glass cottons, and asbestos with respect to chemical inertness, retentivity, and hygroscopicity. Silica is more chemically inert than the so-called resistance glasses, while asbestos may be appreciably dissolved by acids, alkalies, or alkaline solutions of phosphates. Thus in the present work it was found that a Gooch crucible plus its silica cotton mat returned to the same weight (within less than 0.05 mg.) after filtering such precipitates as lead sulfate, silver chloride, or nickel dimethylglyoxime, if the crucible was treated with the appropriate solvent—i. e., 10 per cent ammonium acetate, 6 N ammonium hydroxide, or 6 N hydrochloric acid and then 95 per cent alcohol—and was finally heated again.

Silica cotton possesses good retentivity for precipitates, so that relatively thin filtering mats, weighing only about 50 mg., are required to retain any of the above-mentioned precipitates as well as silver bromide, or cuprous thiocyanate. This appears due, at least in part, to the fineness of the silica fibers which have diameters of the order of  $3 \times 10^{-3}$  mm. The glass cottons examined had fiber diameters about twice this size.

The very low hygroscopicity of silica cotton is a further advantage. In this respect it proved slightly superior to glass cotton and may be much better than asbestos. In comparative tests, similar to those of Hüttig (1), in which Gooch crucibles were heated to 200° C. for one hour, cooled

in a desiccator, and weighed after various intervals of atmospheric exposure, no change in weight (less than 0.03 mg.) was detected in the crucible containing the silica cotton mat during 2.5 hours' exposure, while the crucible having a resistance glass cotton mat gained 0.1 mg. in one hour, and the crucible with a mat of highly purified asbestos gained 0.1 mg. in 30 minutes. When the temperature of heating was increased to 600° C. the crucible containing the silica cotton still showed no detectable gain in weight, while the crucible containing the asbestos gained 0.1 mg. in 10 minutes' exposure. The asbestos may be much more hygroscopic is familiar to all analysts, and is recorded in Hüttig's work (1) in which gain in weight of 0.1, 0.6, 1.2, 2.4, and 3.4 mg. were found for Gooch crucible containing dried asbestos exposed to the atmosphere for 2, 5, 10, 30, and 60 minutes, respectively.

A Gooch crucible is prepared with silica cotton simply by winding a narrow ribbon of the cotton into a flat spiral about 3 mm. thick and of a proper diameter to fit the bottom of the crucible. After pressing into place the cotton felts together considerably and remains in position; however, the crucible should not be carelessly handled. The weight of silica cotton used in a 20-ml. crucible is about 50 mg.

Although the silica cotton is more expensive than glass cotton, little is required, and a crucible once properly prepared and intelligently handled can be used repeatedly with negligible weight changes. On the basis of the authors' experience it appears that a Gooch crucible prepared with silica cotton has most of the advantages of a sintered-glass filter crucible, and in addition can be used at much higher temperatures.

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# A Simplified Combustion Pipet

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SEVERAL improvements in the design of combustion pipets have been made since 1876 when Coquillon (2) proposed the use of an electrically heated platinum spiral for slow-combustion analyses of hydrocarbon mixtures.

Weaver and Ledig (7) suggested the use of a fine platinum spiral in a Pyrex or quartz capillary tube for the analysis of small quantities of combustible gases. Bayley (1) described a pipet into which the gas was admitted through a small platinum jet in the side of the pipet directly onto a heated platinum spiral. He claimed that the danger of explosion was less with this apparatus, since mixing was much better. Matuszak (5) employed a pipet with the upper portion terminating in a cone containing an inverted V-type of platinum coil. Porter and Cryder (6) described a combustion pipet in which the mixture of combustible gas and oxygen was passed through a vertical platinum tube 0.9 mm. in diameter, located within the pipet. The glowing platinum spiral was located just above the opening of the platinum tube.

The commercial type of apparatus usually employs a comparatively wide combustion pipet, the heating element being near the top where the tube may be somewhat constricted. In the proposed pipet the smaller cross section and the arrangement of the heating spiral parallel to the gas flow prob-

ably allow more intimate contact with the gas at the combustion temperature. Carbon monoxide and hydrogen are completely removed before the residual sample of gas, which contains only methane and nitrogen, is passed into the explosion pipet for analysis.

The use of a heating element which can be removed and replaced quickly and conveniently without the necessity of removing the mercury should interest the commercial gas analyst, for whom delays due to repairs may seriously interfere with plant control. The use of an interchangeable ground-glass joint, in addition to facilitating the removal of the platinum spiral, precludes the necessity of replacing or repairing anything more than the broken part, in case of an accident.

## Description of Combustion Pipet

The modified apparatus is shown in Figure 1. The combustion pipet is constructed of a Pyrex glass tube, *A*, to which are sealed two glass side tubes through which pass 20-gage wires, *CB* and *DE*, each consisting of a piece of platinum wire spot-welded to a piece of tungsten wire. The platinum portion is used within the tube and is bent to form a hook at *B* and *E* in order to keep the platinum spiral from slipping off. The tungsten portion of the wire provides a satisfactory means for making a gas-tight seal with the glass. The use of the tungsten wire-glass seal has proved very satisfactory and the authors have experienced no difficulty with the glass cracking at this point. The wire is of sufficient length (over 2 cm.) outside the tube so that it can be soldered to copper leads without danger of the solder's being melted by the heat transmitted from the glowing spiral.

The spiral heating element is made from a 12.5-cm. (5-inch) piece of 26-gage platinum wire and is hooked on at *B* and *E*. The source of current for heating this is 110-volt alternating current which, by means of a transformer, is reduced to about 6 volts and controlled with a small rheostat. Should the platinum coil burn out or break, it can be removed and replaced readily with a pair of narrow tweezers. An interchangeable ground-glass joint, *G*, 19/38, is located at the lower end of tube *A*, providing a means for attaching the 125-cc. flask, *H*. The ground joint is lubricated with a small amount of vaseline and kept tightly closed by means of two springs.

A practice, common with all types of combustion pipets, is to provide a shield for protection of the operator in case of an explosion. For this purpose a wire gauze (16 meshes per 2.5 cm., 1 inch) is placed in a position between the operator and the pipet. This gauze does not materially obstruct the operator's vision and will serve as a protection from flying glass if an explosion should take place.

## Procedure

Air or oxygen may be used for the combustion, though oxygen is preferable as it allows the use of a larger sample. A sample containing 10 to 15 cc. of methane thoroughly mixed with about 85 cc. of oxygen was found to work satisfactorily.

The wire gauze shield was adjusted in place between the operator and the pipet. Then the spiral was heated to a bright yellow color and the combustible gas mixture passed over it at the rate of about 10 to 20 cc. per minute, while controlling the temperature of the spiral (to prevent overheating as the gas burns) by means of a rheostat. The mixture was again led over the spiral at a somewhat higher rate and this procedure was continued until four passages had been made. The gas mixture was then cooled to room temperature by a small air blast and its volume measured before and after removing the carbon dioxide.

The gas analyzed consisted of methane with a small amount of nitrogen present. In the modified Orsat type of apparatus, such as was employed here, hydrogen and carbon monoxide are determined before the methane combustion is made. This proposed pipet was designed primarily to replace the commercial type of methane pipet formerly used and the authors do not recommend its use for combustion of hydrogen or carbon monoxide.

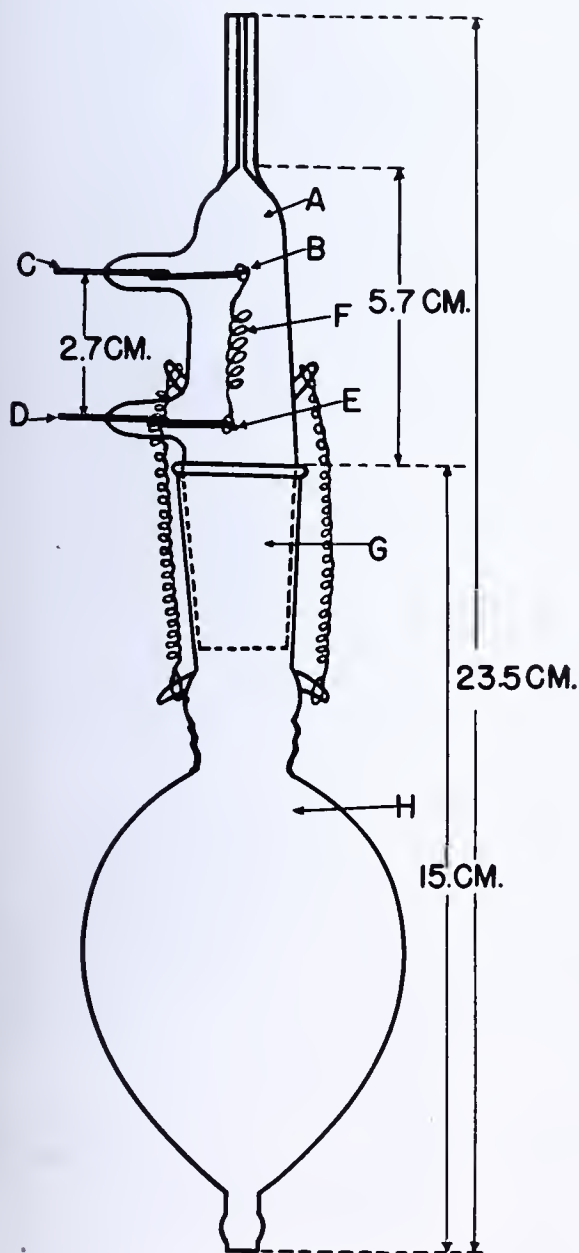


FIGURE 1. DIAGRAM OF PIPET



TABLE I. ANALYSIS OF TYPICAL RESIDUAL FERMENTATION GASES

Sample	Gas Analyzed	Oxygen	Methane
	Cc.	Cc.	%
a	14.6	84.3	79.6
	14.85	82.15	80.3
b	13.8	84.4	83.1
	13.8	84.0	83.1
	9.8	84.1	83.4
c		Air	
	5.0	95.0	95.9
	5.0	95.0	98.1
d	9.0	91.0	91.2
	9.0	91.0	91.2

Using either air or oxygen for the combustion, the data given in Table I show the analysis of typical residual fermentation gases, after the oxygen, carbon dioxide, and hydrogen had been removed. Generally, oxygen yielded closer duplicate results than air.

### Discussion and Conclusions

In the use of the slow-combustion pipet the recommended procedure is to make several passes of the gas over the hot coil (3, 4). To determine the efficiency of this combustion pipet, after removing the carbon dioxide produced during the first four passes, two additional passes of the gas were made. Results of these additional passes showed 0.91 to 2.67 per cent

(average, 1.61 per cent) residual methane left after the first four passes. These percentages are based on the original sample and conform to plant control practice.

The apparatus described in this paper was constructed with the idea of incorporating several desirable features in one combustion pipet and at the same time keeping the construction simple and inexpensive. These features are: (1) the location of the heating spiral in a tube of comparatively small cross-sectional area; (2) the attachment of the spiral in such a manner that it can be quickly and easily removed and replaced; and (3) the use of a standard ground joint just below the heating coil. This combination of features is a simplification of the apparatus hitherto used in routine gas analysis.

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## A Flask for Efficient Stirring

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MUCH attention has been paid to different kinds of stirrers, but very little to the type of container which is by far the more important. After a considerable variety of stirrers had been tried, all with little benefit because swirling in round flasks kept the heavy particles in an outside belt, the author observed a marked improvement upon changing the shape of the container. In particular, vertical creases in the side of the flask had a pronounced effect.

As many as four creases, each 7.5 to 10 cm. (3 to 4 inches) long by 0.6 to 2.5 cm. (0.25 to 1 inch) in depth, tapering in width from 0.3 cm. (0.125 inch) at the innermost part to 3.75 cm. (1.5 inches) at the circumference, have been made in flasks whose capacity varied from 0.5 to 2 liters. The depth of the crease was not proportioned to the size of the flask but depended partly on the speed with which the stirrer was to be operated. For instance, an 0.5-liter flask in which deep wedges had been sunk in the circumference appeared as if sectioned into four parts about a central portion in which the stirrer rotated at high speed in order to agitate the mixture. Moderately deep creases break up the average swirling but may fail to prevent the funnel-shaped depression about the stirrer when it is operated at high velocity.

In operation a stirrer of the propeller type with blades pitched at about a 45° angle has proved satisfactory. The mixture is usually pushed downward against the bottom of the flask and up between the sections, from whence it falls again onto the stirrer. With thick slurries the stirrer is driven faster and faster until the mixture moves readily. The agitation in such cases is remarkable.

Observations on the efficiency of stirring were usually made with a mixture of sea sand and water. With the ordinary flask the sand would collect in belts and layers, depending on the speed of rotation and the position and shape of the stirrer. These results were contrasted with the even dis-

persion obtained in the new flask. In making sodium sand for use in reactions with sodium in progress in this laboratory, the particles were more uniform and were a third to a fourth the diameter of those obtained in round flasks. Reaction mixtures so thick that the stirrer rotated without appreciable agitation in the ordinary flask were readily mixed, particularly if the speed were increased. A great advantage in all cases was a continued improvement in the results as the rotation velocity was increased.

Previously, comment has been made (1) on an improvement in the dispersion of sea sand in water when a square bottle was used. Such containers, however, are apt to crack when heated, have corners in which solid particles lodge, and will allow a funnel to form around the stirrer at high speeds. Rectangular containers overcome the swirling but not all of the pocketing. The author has, however, had very satisfactory results making sodium sand in rectangular apparatus. Baffles placed in beakers also have pockets in which heavy particles can collect. Most of these containers cannot be used readily with experiments in which the mixture must be refluxed or kept in an inert atmosphere. Fortunately the ordinary flask with its rounded bottom, so helpful in avoiding pockets, and its partially closed top, can be converted into an ideal container for stirring with the changes noted above.

Construction is relatively easy for any competent glass blower, the principal precaution being good annealing.

### Acknowledgment

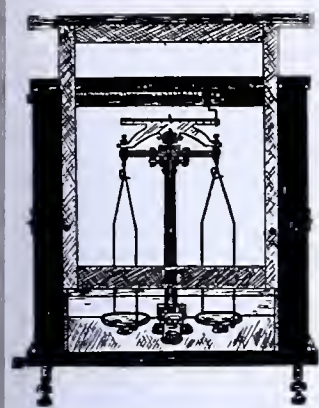
The author is indebted to Mr. Wayringer for his cooperation in constructing different shaped stirrers and these flasks.

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RECEIVED November 19, 1938.





# Microchemistry

## Microdetermination of Fluorine by Thorium Nitrate Titration

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THE Willard and Winter method for determining fluorine (11) with the use of sodium alizarin sulfonate indicator as proposed by Armstrong (2) has been modified recently as follows: by Hoskins and Ferris (8) who introduced the use of a buffer of monochloroacetic acid; by Armstrong (1) who titrated fluoride in an aqueous solution rather than in an alcoholic solution, and used silver perchlorate to remove interfering chlorides; and by Churchill, Bridges, and Rowley (3) who eliminated the effect of phosphate by a double distillation. Rowley and Churchill (10) applied the aqueous titration to the determination of quantities of 1 to 50 mg. of fluorine. Eberz, Lamb, and Lachele (6) studied the titration in alcoholic solution of quantities of 100 to 150 micrograms of fluorine. [Dahle and associates (5) have recently studied a "back-titration procedure" as suggested to them by W. S. Allen.]

The microdetermination of fluorine according to Armstrong gave an average error of  $-2.0$  per cent in the recovery of 2.0 micrograms of fluorine (1) and "the lower limit seems to be in the vicinity of 0.4 gamma." The method (1) appears particularly advantageous also in that the quantities of reagents and the analytical sample may be reduced to a minimum. The results presented herein, however, show that the titration is less sensitive than Armstrong reports. One of the most disturbing features is an appreciable blank titration which tends to fix the minimum quantity of total determinable fluorine appreciably higher than Armstrong suggests. The minimum quantity actually titrated in aliquots, with reasonable accuracy, was found to equal about 5.0 micrograms.

### Limit of Accuracy of the Titration

Titration results with pure fluoride solutions using Armstrong's method, with the use of the Hoskins and Ferris buffer, are given in Table I. The determination of the end point was found to be difficult and frequently uncertain. For best results the color of the unknown and standard was judged with the vial resting on a dull white surface, in light produced by a monochromatic daylight bulb. The end point was scarcely sensitive to a variation of less than 0.030 to 0.050 cc. of the thorium nitrate, equivalent to 0.15 to 0.25 microgram of fluorine. In order to obtain the high recovery which Armstrong reports, it is necessary to titrate much closer than this—i. e., with an error equal to about 0.04 microgram of total fluorine (1) or even less, since aliquots of the total are titrated.

As shown in Table I there is an average blank titration of 0.355 cc. which represents thorium nitrate required to produce the pink colored lake formed following the fluorine-thorium nitrate reaction and used as the end point. It was not thought desirable to have this titration blank equal to more than a third of the total actual titration figure. This in itself restricts the method to the determination of a minimum of about 10.0 micrograms of total fluorine under the conditions that the aliquot titrated is not less than  $\frac{1}{5}$ —i. e., at least 2 micrograms are taken for the actual titration, and 3 or 4 aliquots are titrated to obtain an average titration figure.

TABLE I. TITRATION OF AQUEOUS FLUORIDE SOLUTIONS WITH THORIUM NITRATE

Fluorine Added Gamma	Th(NO <sub>3</sub> ) <sub>4</sub> Required for 1/10 Aliquot <sup>a</sup> Cc.	Total Fluorine Titrated Gamma	Total Fluorine Found Gamma	Error in Fluorine Found Gamma	Recovery %
10.0	0.200	1.04	10.4	+0.4	104.0
10.0	0.247	1.28	12.8	+2.8	128.0
11.3	0.232	1.21	12.1	+0.8	107.1
11.3	0.216	1.13	11.3	0.0	100.0
20.0	0.369	1.92	19.2	-0.8	96.0
20.0	0.408	2.12	21.2	+1.2	106.0
50.0	1.038	5.40	54.0	+4.0	108.0
50.0	1.000	5.20	52.0	+2.0	104.0
68.0	1.354	7.04	70.4	+2.4	103.5
68.0	1.342	6.98	69.8	+1.8	102.6
100.0	1.940	10.09	100.9	+0.9	100.9
100.0	1.831	9.52	95.2	-4.8	95.2
100.0	1.873	9.74	97.4	-2.6	97.4

<sup>a</sup> Net titration after subtracting blank. Titration figures for five blanks equaled 0.303, 0.363, 0.313, 0.358, and 0.360 cc.; av., 0.355 cc. 1 cc. of Th(NO<sub>3</sub>)<sub>4</sub> = 5.2 gamma of fluorine.

For best results the actual titration was carried out on at least 5 to 10 micrograms of fluorine, requiring from 1.5 to 3.0 cc. of the thorium nitrate. These limits are more in keeping with the limits of accuracy found in the actual titration and with the size of the blank titration figure.

### Effects of Evaporation in Glass or Porcelain

Table II gives results obtained from evaporation on a water bath of pure fluoride solutions, using glass, porcelain, and platinum containers. The recoveries are generally low with evaporation in glass and porcelain. The addition of the buffer did not give the characteristic bright yellow color to these solutions. On adding thorium nitrate the pink color of the end point appeared quite as usual but the fluoride-thorium nitrate reaction apparently was interfered with in view of the low titration figures. These results show the need of avoiding the use of porcelain and glass containers for the



TABLE II. COMPARISON OF GLASS, PORCELAIN, AND PLATINUM CONTAINERS FOR EVAPORATION OF ALKALINE SOLUTIONS OF SODIUM FLUORIDE

(150-cc. volumes evaporated, made to 10 cc., 1/10 aliquot titrated)								
Glass				Porcelain			Platinum	
Fluorine Added Gamma	Th(NO <sub>3</sub> ) <sub>4</sub> required for 1/10 aliquot Cc.	Error in total fluorine Gamma	Recovery %	Th(NO <sub>3</sub> ) <sub>4</sub> required for 1/10 aliquot Cc.	Error in total fluorine Gamma	Recovery %	Th(NO <sub>3</sub> ) <sub>4</sub> required for 1/10 aliquot Cc.	Error in total fluorine Gamma
0.0	0.340	....	..	0.319	....	...	0.385	...
0.0	0.319	....	..	0.335	....	...	0.356	...
0.0	0.358	....	..	0.329	....	...	0.413	...
10.0	0.470	-5.4	54.0	0.531	+0.2	102.0	0.626	+1.9
10.0	0.413	-6.3	37.0	0.486	-2.1	79.9	0.572	-0.7
50.0	1.125	-10.7	78.6	1.239	-4.5	91.0	1.309	-3.7
50.0	1.098	-12.0	76.0	1.138	-9.5	81.0	1.450	+2.3
100.0	2.226	-5.7	94.3	1.728	-29.9	70.1	2.416	+1.7
100.0	2.188	-12.6	87.4	2.114	-10.7	89.3	2.410	+1.3
150.0	3.300	-2.0	98.6	2.992	-16.8	88.8	3.377	-0.3
150.0	3.110	-10.6	92.9	3.084	-12.2	91.8	3.441	+2.9

evaporation of the alkaline fluoride distillates. The cause of this interference was not determined. It indicates strikingly the extreme sensitivity of this titration to slightly modified conditions.

### Addition of Silver Sulfate to Distilling Flask

Hoskins and Ferris (8) reported an effect of chloride on the alcoholic titration; Armstrong (1) found chloride to interfere in both aqueous and alcoholic titration of fluorine. The author's data show a similar interference beginning at about 4.0 mg. of chlorine per cc..

Armstrong (1) eliminated chloride from the distillate by a rather involved procedure requiring precipitation with silver perchlorate, filtering, redistilling the filtrate, and evaporating the second distillate which is treated with activated charcoal and filtered again before making up to volume. Eberz, Lamb, and Lachele (6) add silver perchlorate solution to a solution of the ash to be distilled, carefully avoiding any excess of silver salt. This ash mixture is dried and transferred to the distilling flask. They found distillation in the presence of silver chloride precipitate "entirely satisfactory, not giving trouble by bumping, holding back fluorine, or releasing the chloride which it is desired to eliminate" (6).

The precipitation of chloride in the distilling flask as the silver salt recommends itself as a simple and effective procedure and had been studied prior to the appearance of the article by Eberz *et al.* (6). The recovery of fluorine was satisfactory (Table III). Although bumping at first proved troublesome, this was partially overcome by the use of solid silver sulfate added directly to the ash solution or to a first distillation concentrate. A less flocculent precipitate was formed under these conditions than when the silver salt was added in a solution. Bumping is eliminated to some extent also in the steam-distillation procedure where the precipitate is kept continuously agitated by steam entering the mixture. It does not appear necessary to avoid a slight excess of silver sulfate. If a second distillation is to be made the required silver sulfate is added for the second distillation.

### Application of Method to Biological Materials

As has been pointed out by Dahle and Wichmann (4) and by Hoffman and Lundell (7), considerable uncertainty may still surround the method of separation of fluorine by volatilization in the presence of perchloric or sulfuric acid. It is desirable, therefore, to report satisfactory results (average error about  $\pm 3.0$  micrograms) using perchloric acid and the general technique of Armstrong (1) and of Hoskins and Ferris (8), in the recovery of fluoride added to the distilling flask. The distilling blank titration equals 0.400 to 0.500 cc. (these figures include titration blank of 0.20 to 0.30 cc. previously discussed), owing perhaps to fluorine in the reagents or to

volatilized perchloric acid. It was not found possible to change this blank appreciably by collecting several volumes of distillate from the same sample of perchloric acid or by heating the acid to 170° C. and then collecting 150-cc. samples of distillate at 140° C. Perchlorate ion was found to affect the titration when equal to about 2.0 to 4.0 mg. per cc.

As applied to the determination of the fluorine in biological material, the total body of experimental test rats, for example (9), the procedure was as follows:

The animal body was autoclaved at 120° C. (15 pounds) for about 0.5 hour, dried first in a warm air bath and then in an oven at 100°, moistened with 5 per cent magnesium acetate (12), and ashed in a muffle furnace at 500° C. An aliquot of the ash, equaling approximately 0.50 gram or less, was taken for the fluorine determination.

TABLE III. ELIMINATION OF EFFECT OF CHLORIDE BY ADDITION OF SILVER SULFATE

(Sodium chloride and silver sulfate added to distilling flask, 150-cc. distillate collected, evaporated, made to 5 cc., 1/5 aliquot titrated)

Fluorine Added Gamma	NaCl Added Gram	Ag <sub>2</sub> SO <sub>4</sub> Added Grams	Th(NO <sub>3</sub> ) <sub>4</sub> Required for 1/5 Aliquot Cc.	Total Fluorine Found Gamma	Error in Fluorine Found Gamma	Recovery %
20.0	0.0	0.0	1.228	20.7	+0.7	103.5
20.0	0.0	0.0	1.341	24.0	+4.0	120.0
20.0	0.0	0.0	1.499	21.0	+1.0	105.0
20.0	0.0	0.0	1.396	19.1	-0.8	95.5
20.0	0.1	0.0	1.660	25.0	+5.0	125.0
20.0	0.1	0.0	1.680	25.4	+5.4	127.0
20.0	0.2	0.0	1.725	26.5	+6.5	127.5
20.0	0.2	0.0	1.718	26.3	+6.3	126.5
40.0	0.4	0.0	2.324	46.5	+6.5	116.2
40.0	0.4	0.0	2.456	49.8	+9.8	124.5
20.0	0.1	0.3	1.358	23.3	+3.3	116.5
20.0	0.2	0.6	1.343	21.2	+1.2	106.0
25.0	0.2	0.6	1.364	22.5	+2.5	110.0
50.0	0.2	0.6	2.405	48.6	-1.4	97.2
50.0	0.2	0.6	2.525	51.6	+1.6	103.2
100.0	0.4	1.2	2.421	97.8	-2.2	97.8
100.0	0.4	1.2	2.529	103.3	+3.3	103.3

TABLE IV. ANALYSIS OF BONE ASH

Sample Weight Gram	Fluorine Added Gamma	Th(NO <sub>3</sub> ) <sub>4</sub> Required for Aliquot Cc.	Total Fluorine Found Gamma	Recovery of Added Fluorine Gamma	Fluorine in Sample %
0.500	0.0	1.729	59.5	..	0.0119
0.500	0.0	1.695	60.6	..	0.0121
0.500	50.0	2.632	108.4	48.4	0.0120
0.500	50.0	2.596	106.6	46.6	0.0120
0.500	50.0	2.661	109.9	49.9	0.0120
0.040	0.0	2.108	77.3	..	0.1932
0.040	0.0	2.181	80.7	..	0.2017
0.040	0.0	2.735	92.5	..	0.2312
0.040	0.0	2.552	98.1	..	0.2452
0.020	0.0	2.915	100.0	..	0.5000
0.020	0.0	2.674	103.8	..	0.5190
0.020	0.0	3.215	112.7	..	0.5635
0.020	0.0	3.246	114.0	..	0.5200



The ash sample was placed in a 50-cc. Claissen flask together with 5 cc. of 60 per cent perchloric acid, 0.1 gram of pure silica, 10 cc. of distilled water, and two glass beads. The mixture was steam-distilled at a temperature of 138° to 142° C. receiving the distillate in a solution kept definitely alkaline to phenolphthalein, and continuing the distillation until 150 cc. were collected. The distillation should be completed in about 30 minutes. The alkaline distillate was placed in a platinum dish, evaporated on the water bath to about 5 cc., neutralized with dilute hydrochloric acid, and made up to 10 cc. Four or five 1-cc. aliquots were titrated in a manner essentially as described by Armstrong (1). Some results obtained in applying the above procedure to bone and body ash are given in Table IV.

50 to 100 micrograms of added fluorine varied from 80.0 to 125.0 per cent. Doubtless the quantity of fluorine dealt with is too small, but a larger analytical sample would require increased quantities of reagents, a larger flask, and perhaps other modifications, which may affect the distillation (5) and alter the titration conditions.

No attempt has been made to introduce such modifications as appear to be necessary from the above results, in order to apply the method successfully to substances such as milk powders.

TABLE V. ANALYSIS OF SKIM-MILK POWDER

Sample Weight Grams	Mg(Ac) <sub>2</sub> Gram	Ag <sub>2</sub> SO <sub>4</sub> Grams	Fluorine Added Gamma	Aliquot Titrated	Th(NO <sub>3</sub> ) <sub>4</sub> Required for Aliquot Cc.	Total Fluorine Found Gamma	Recovery of Added Fluorine Gamma	Fluorine in Sample Gamma P. p. m.	
0.0	0.0	0.0	0.0	1/5	0.453	...	...	..	..
0.0	0.0	0.0	0.0	1/5	0.403	...	...	..	..
0.0	0.0	0.0	0.0	1/5	0.383	...	...	..	..
0.0	0.0	0.0	0.0	1/5	0.471	...	...	..	..
0.0	0.5	2.0	0.0	1/5	0.643	8.9	...	..	..
0.0	0.5	2.0	0.0	1/5	0.623	8.2	...	..	..
0.0	0.5	2.0	100.0	1/10	2.614	108.6	100.1	..	..
0.0	0.5	2.0	100.0	1/10	2.586	107.2	98.7	..	..
0.0	0.5	2.0	50.0	1/5	2.405	57.1	48.6	..	..
0.0	0.5	2.0	50.0	1/5	2.525	60.1	51.6	..	..
50.0	0.5	2.0	...	1/5	2.256	45.4	...	36.9	0.73
50.0	0.5	2.0	...	1/5	1.668	30.6	...	22.1	0.44
50.0	0.5	2.0	...	1/5	1.929	37.1	...	28.6	0.57
50.0	0.5	2.0	100.0	1/10	3.694	162.6	124.9	(29.2)	..
50.0	0.5	2.0	100.0	1/10	2.840	111.0	81.3	(29.2)	..
50.0	0.5	2.0	50.0	1/10	2.453	100.6	62.9	(29.2)	..
50.0	0.5	2.0	50.0	1/10	2.146	85.2	47.5	(29.2)	..

In the majority of these determinations 50.0 to 100.0 micrograms were adopted as the range of determinable fluorine and 0.50 gram or less of ash constituted the analytical sample. It was intended to keep the size of the analytical sample as small as possible to avoid interfering elements. The recovery of fluorine in the presence of these small quantities of ash was within the limits of error found for pure fluoride solutions added to the distilling flask. Duplicate determinations agreed within 2.0 to 6.0 micrograms of fluorine. In bone and tooth ash or total body ash the only interfering substance would appear to be phosphate. Its effect was eliminated by a double distillation, as proposed by Churchill *et al.* (3) when the sample exceeded 0.1 gram. [An interference of phosphate (PO<sub>4</sub>) on the titration was noted at a concentration of about 1.0 microgram per cc.]

In the determination of fluorine in foods and biological materials where the quantities of fluorine present may be 10 p. p. m. or less, more serious difficulties are encountered. The size of sample which will yield a determinable quantity of total fluorine may be extremely large and may include a large yield of ash containing large quantities of interfering chlorides and phosphates, and perhaps other interfering agents. An effort was made to apply the method outlined to dried milk powder which is extremely low in fluorine and high in total ash containing considerable phosphate and chloride. In limiting the determinable fluorine to a minimum of 50 micrograms, at least 100 grams of a material containing 0.5 to 1.0 p. p. m. of fluorine must constitute the analytical sample. Total ash from 100 grams of milk powder is excessive for a 50-cc. flask and 5 cc. of perchloric acid are not enough to keep the ash in solution for distilling. Even on reducing the sample to 50 grams as was done for the data reported in Table V, 10 cc. of perchloric acid, instead of the recommended 5 cc., were required. Under these modified conditions 50-gram duplicate samples varied as much as 14 micrograms of fluorine in an average of approximately 30 micrograms of total fluorine determined. The results for the same sample showed 0.44 to 0.73 p. p. m. of fluorine present. Recovery of

## Summary

The microdetermination of fluorine by titration in aqueous solution with thorium nitrate according to Armstrong's latest technique did not give the high degree of accuracy obtained by Armstrong. The recovery of fluoride added to bone ash in 50.0- to 100.0-microgram quantities varied about  $\pm 5.0$  micrograms from the total added. Duplicate samples of bone and tooth ash agreed within 2.0 to 6.0 micrograms of total fluorine, where a total of 50.0 to 100.0 micrograms of fluorine were determined, the size sample equaling not more than 0.5 gram of ash. An attempt to apply the method to the analysis of a material such as milk powder containing less than 1.0 p. p. m. of fluorine was not successful.

The necessity of avoiding glass or porcelain containers in evaporation of alkaline fluoride distillates, previous to titration with thorium nitrate, is indicated. A method for the prevention of volatilization of chloride, by precipitation with silver sulfate added to the distilling flask, was found satisfactory.

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# Microdetermination of Alkoxy Groups

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**A modified and improved apparatus and procedure for the quantitative microdetermination of alkoxy groups are described. They are equally well adapted to solids, semiliquids, and liquids with boiling points above, at, or below that of hydriodic acid, irrespective of the number of alkoxy groups. Accurate analytical figures are obtained by virtue of better solution of the substance, more gradual and longer heating, and thorough absorption.**

THE value of an accurate and generally applicable method for the microdetermination of the alkoxy group is self-evident, yet many analysts report difficulties in the estimation of substances containing more than one such group.

In the course of thirteen years of microanalytical experience, many hundreds of alkoxy determinations have been performed in this laboratory. The whole field has been investigated and improvements in technique and apparatus have been devised in order to overcome discrepancies and difficulties often reported.

The original Zeisel methoxyl macromethod, as adapted and modified for microdeterminations by Pregl (13), consisted in heating the substance with hydriodic acid, driving off the alkyl iodide with carbon dioxide, absorbing it in alcoholic silver nitrate, and estimating the silver iodide gravimetrically. Later Vieböck and Brecher (16) shortened the last part of the procedure by employing a volumetric titration of the iodine, which had distilled as alkyl iodide.

The modified apparatus of Rigakos (14) has been used in the author's laboratory since 1931. His improvement consists in the introduction of a ground-glass joint between the reaction flask and the outlet tube, and of a capillary leading from the side arm near the bottom of the reaction flask. Exactly the same modification of the apparatus was described much later by Neumann (11) for highly methylated carbohydrates. Clark has described (3) an apparatus having ground-glass joints and a capillary side arm, which can be used for macro- and microdeterminations. Chinoy (2) has also constructed a modified apparatus with a ground joint fitting into the reaction flask and with an extension ending in a glass ladle, which facilitates the introduction of the sample. These improvements have been applied to solid and sirupy substances and to liquids whose boiling points are above that of hydriodic acid.

Colson (4) has devised an apparatus for liquids having boiling points lower than that of the hydriodic acid, consisting of a vertical tube filled with small glass beads, which are wetted with hydriodic acid, connected above the reaction flask. He also connects in the train two washing tubes to entrap any hydriodic acid that might have distilled over because of its initial high specific gravity (1.96).

Lieff, Marks, and Wright (10) have described a modified apparatus which, they state, is more advantageous for the titration method. The Pregl type of receiver is replaced by an absorption tube containing four "pockets," the construction of which requires great care, and is attached to the outlet tube of the Pregl type of apparatus by a ground-glass joint in an inclined position.

Lately, in the author's laboratory an apparatus has been constructed (Figure 1) which has been found highly satisfactory for solids as well as for liquids with boiling points above, at, and below that of the hydriodic acid. There is a ground joint between the reaction flask and the outlet tube, as described by Rigakos (14). The ascending tube has three small bulbs, *C*, which unfailingly complete the condensation of any hydriodic acid, evaporated because of the heating, or possibly carried up mechanically by the carbon dioxide stream. These three bulbs, placed at suitable distances apart, also serve to cool the alkyl

iodide entering the absorbent and eliminate the necessity of any cooling of the latter, such as recommended by White and Wright (18). Surrounding the bulbous portion of the ascension tube is a water condenser.

It is important in the determination of alkoxy groups that there be thorough absorption, and, in the titrimetric method, complete oxidation of the alkyl iodide to the iodate. This is achieved by means of a long and slow passage of the alkyl iodide through the absorbing liquid. For this purpose a glass spiral, consisting of about twelve turns, was devised and attached to the outlet tube (*D*, Figure 1), which is immersed in the absorbent contained in a modified Kahovec (8) type of receiver. The bubbles enter the absorbent through a very small opening, *E*, and are forced to traverse the entire length of the glass spiral.

## Experimental

Solid substances, previously dried and ground, are weighed by difference on the microbalance and placed on the bottom of the previously dried reaction flask, preferably using a long-handled charging tube.

For the weighing of semisolids, substances of sirupy consistency, and nonvolatile liquids, a small glass cup, about 4 to 5 mm. in diameter and height, which fits conveniently into the neck of the reaction flask, is used. This cup can also be used for solids.

A piece of glass in the shape of a semicylindrical boat or trough with open ends, made from glass tubing of suitable diameter by cutting it lengthwise, or a piece of platinum sheet molded to a boatlike shape also serves the purpose.

A few crystals of the purest phenol and 6 to 10 drops of acetic anhydride (or still better, propionic anhydride) are added and the flask is agitated in order to effect solution. If the substance is not completely dissolved the reaction flask is carefully heated in a water bath (or over a very small flame) to about 60° to 80° C., avoiding excessive heating. If complete solution still does not occur, a little more of the mixed solvent is added until all is dissolved, and the solution is then cooled. Since this extra solvent will considerably lower the eventual concentration of the hydriodic acid, 0.3 to 0.5 ml. extra of hydriodic acid (specific gravity, 1.96) must be added to restore its original specific gravity.

The reaction flask is then cooled, a few Alundum beads (size 16) are inserted, and about 2 ml. of hydriodic acid (specific gravity, 1.7) are added dropwise from a pipet, rotating the neck of the reaction flask to wash down any small particles of substance that might have adhered thereto. The washing tube has already been charged in the usual manner with 5 per cent cadmium sulfate solution and either a suspension of red phosphorus or a solution of sodium thiosulfate.

For the gravimetric determination, the usual Pregl type of receiver is charged with 2 ml. of alcoholic silver nitrate employing a straight outlet tube. For the more convenient volumetric determination of Vieböck and Brecher (16), the Kahovec (8) type of receiver is used, containing 4 to 5 ml. of glacial acetic acid-sodium acetate solution to which 6 to 8 drops of bromine are added. The glass spiral is carefully inserted into this solution, the reaction flask is connected as quickly as possible, and the side arm is attached to the source of carbon dioxide, the flow of which is reduced to a slow stream. The adjustment of the stream is best achieved by inserting between the side arm and the carbon dioxide generator a stopcock having a fine groove, similar to that used in the Dumas micromethod.

**SOLIDS AND NONVOLATILE SUBSTANCES.** The reaction flask is allowed to stand at room temperature for about 30 minutes, after which a small flame is placed under the flask and so regulated that the temperature of the solution remains below the boiling point for another 30 minutes. The flame is then raised slowly and the solution is brought to the boiling point, and maintained at that temperature for 1 to 2 hours—in some instances even longer. About 15 minutes prior to the completion of the determination, the rate of carbon dioxide inflow is increased in order to drive traces of alkyl iodide into the receiver.

The gravimetric determination is performed in the usual manner. Using the titrimetric method, which is preferred, the receiver is emptied and its contents are washed into a ground glass-stoppered Erlenmeyer flask (100 to 125 ml.) containing 0.1 to 1 gram of sodium acetate, which has been completely dissolved in a minimal volume of water (a 5 to 10 per cent sodium acetate solution may be used). The excess free bromine is now de



stroyed by adding a few drops of formic acid while whirling the flask several times. The flask is allowed to stand for a few minutes, then stoppered, and shaken well in order to remove the last traces of bromine from the vapor phase as well as from the solution. If, after this treatment, the solution is not completely decolorized, another drop of formic acid should be added with shaking. The usual amount of potassium iodide is added, the solution is acidified with 10 per cent sulfuric acid, the flask is again stoppered, and the solution is whirled. In case of a high methoxyl value, as evidenced by the intensity of the color of the iodine liberated, the standing time is extended to 10 to 15 minutes, instead of the usual 5 minutes, before titrating with the standard thiosulfate.

**VOLATILE LIQUIDS** are weighed in a small glass cup with a round-in stopper, or in a capillary tube about 2 mm. in width and 10 to 12 mm. in length. After the substance has been introduced into the capillary and centrifuged, the open end is sealed, and the tube is cooled and weighed.

The capillary is now cut just above the liquid level and both halves are dropped into the reaction flask, which has been previously charged with phenol, propionic anhydride, and a few granules of Alundum. Two milliliters of hydriodic acid are added and the flask is connected to the train as quickly as possible. The carbon dioxide stream is adjusted to a slow flow, and the reaction is allowed to proceed at room temperature for 30 to 40 minutes, with water running through the condenser.

A very small flame is then placed under the reaction flask and the heat gradually increased at such a rate that ebullition commences at the end of about an hour. Active boiling is maintained for a further period of about one hour, or even longer, in some cases of high methoxyl value.

The condenser is now emptied, and the carbon dioxide inflow is increased in order to drive the last traces of alkyl iodide into the absorbent, taking about 15 minutes to complete this procedure. The last step of the determination is the same as for nonvolatile substances.

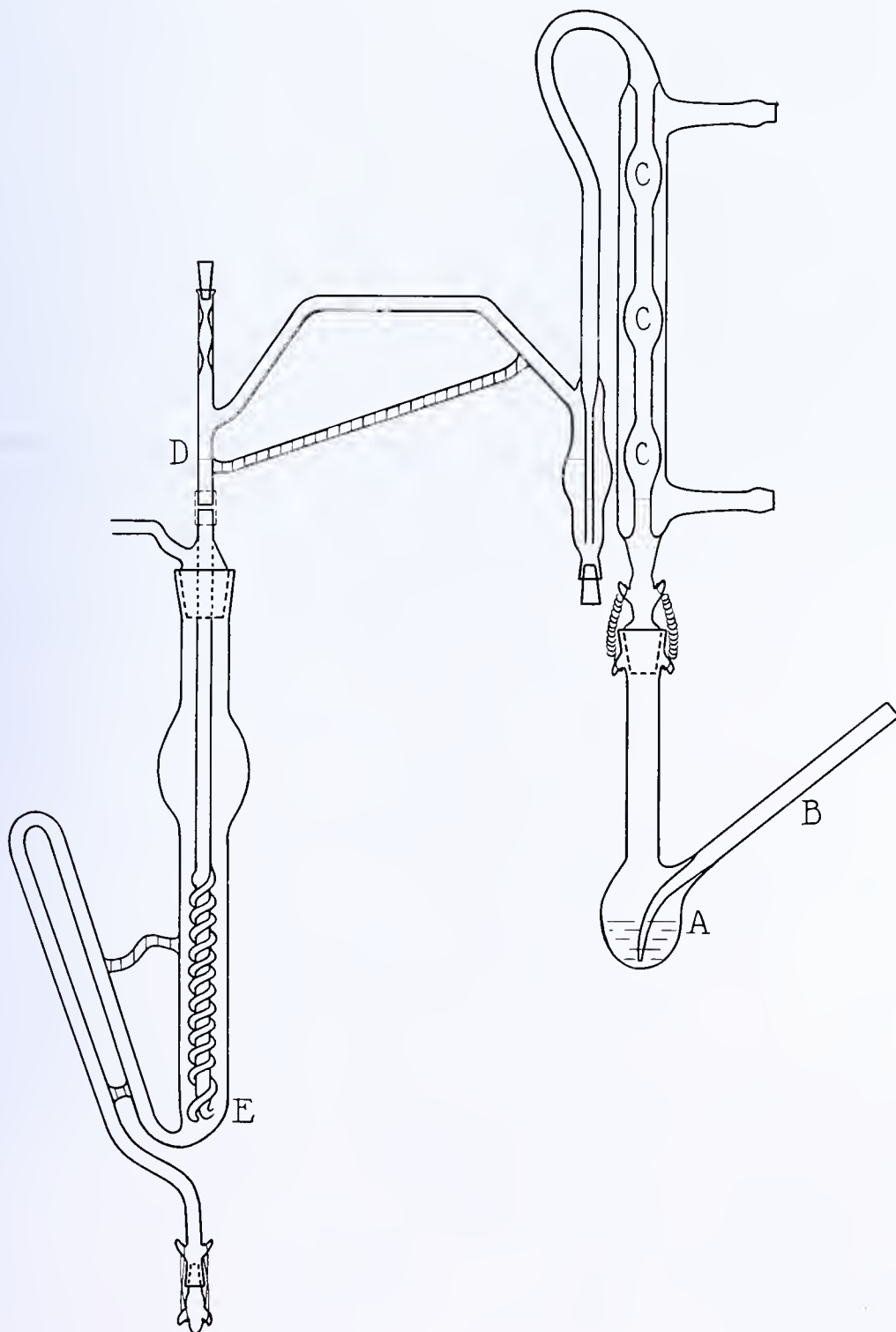


FIGURE 1. DIAGRAM OF APPARATUS



TABLE I. DETERMINATION OF METHOXYL

No.	Compound	Formula	Methoxyl Groups per Molecule	Weight	Vol. of 0.01	Methoxyl Found	Methoxyl Calculated
				of Sample <i>Mg.</i>	<i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (Cor.) <i>Ml.</i>		
1	Heptaacetyl N-acetyl chondro- sin methyl ester	C <sub>29</sub> H <sub>41</sub> O <sub>19</sub>	1	3.795	3.19	4.11	4.09
2	Methyl ester of diacetone- galacturonic acid	C <sub>13</sub> H <sub>20</sub> O <sub>7</sub>	1	3.982	8.32	10.79	10.76
3	Pentamethyl methylgalactu- ronidorhamnoside methyl ester	C <sub>19</sub> H <sub>34</sub> O <sub>11</sub>	7	3.227	30.92	49.57	49.54
4	Methylglycoside of hexamethyl- aldobionic acid methyl ester	C <sub>20</sub> H <sub>36</sub> O <sub>12</sub>	8	2.719	27.60	52.68	53.00
5	Methylglycoside of hexa- methyl-6-glucosidogalactose	C <sub>19</sub> H <sub>36</sub> O <sub>11</sub>	7	3.132	29.77	49.30	49.30
6	Methylglycoside of hepta- methyl-6-glucosidogalactose	C <sub>20</sub> H <sub>38</sub> O <sub>11</sub>	8	3.001	31.91	54.97	54.60
7	Nonamethyl glucosidosorbitol	C <sub>21</sub> H <sub>42</sub> O <sub>11</sub>	9	3.497	39.41	59.08	59.32
8	Pentamethylsorbitol	C <sub>11</sub> H <sub>24</sub> O <sub>6</sub>	5	3.341	39.70	61.44	61.44
9	Pentamethylsorbitol	C <sub>11</sub> H <sub>24</sub> O <sub>6</sub>	5	2.695	31.93	61.25	61.44
10	Tetramethyl methylglucoside	C <sub>11</sub> H <sub>22</sub> O <sub>6</sub>	5	2.914	34.88	61.88	62.00

Discussion

The experiences of several investigators, with regard to the reliability of the alkoxy-group microdetermination, seem rather divergent.

Friedrich (5) states that the method is very accurate if the hydriodic acid is pure, and that in some cases the substance must be brought into solution before adding the hydriodic acid; otherwise the methoxyl groups split only partially, or not at all. As a rule, it is sufficient to add the solvent.

Ware (17) reports that, if the substance contains more than two methoxyl groups, the hydriodic acid (specific gravity, 1.7) should be replaced by hydriodic acid (specific gravity, 1.96) in order to get reliable figures, and she uses a correction of 0.12 mg. for 2 ml. of the alcoholic silver nitrate solution as suggested by Friedrich (6).

According to Bruckner (1) the claim of Ware is actually due to the incomplete solution of special substances in phenol and acetic anhydride, or in some instances, phenol and pro-

pionic anhydride. He erroneously thinks that the quantitative splitting of the methoxyl by the hydriodic acid is not related to the number of the methoxyl groups, but rather to their position in the molecule and to the specific behavior of the substance. In the case of highly methylated carbohydrates, and frequently with well-known crystalline methylated sugars, Neumann (11) mentions that methoxyl values which are 1 to 2 per cent low have often been reported, and attributes this discrepancy to the fact that

the reaction flask is heated over a free flame and the substance in the flask is more or less "caked." According to him, this caked portion of the substance does not react with the hydriodic acid, and the variation in the degree of caking is responsible for the nonreproducibility of values obtained on the same sample, especially with polymeric carbohydrates. He, therefore, employs an oil bath with gradual elevation of the temperature in order to circumvent this effect.

The modified apparatus and procedure described in this paper are calculated to ensure greater accuracy in the alkoxy microdetermination. Complete solution of the substance is one of the requisites for correct results. Caking does not take place if the substance is properly dissolved.

Bruckner (1) obtained correct data in some cases without the use of any solvent, but it is generally agreed that complete solution of the substance is necessary. Pregl (13), Niederl (12), and Kuhn and Roth (9) mention solubility tests before the addition of the hydriodic acid, but this is obviously not feasible when only a small amount of substance is avail-

TABLE II. DETERMINATION OF METHOXYL

No.	Compound	Formula	Boiling Point ° C.	Methoxyl Groups per Molecule	Weight	Vol. of	Meth- oxyl Found	Meth- oxyl Calcu- lated
					of Sample <i>Mg.</i>	0.01 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> <i>Ml.</i>		
11	Trimethyl xylulose	C <sub>8</sub> H <sub>16</sub> O <sub>5</sub>	64 at 0.25 mm. Hg	3	3.458	32.36	48.38	48.45
12	Trimethyl xylulose	C <sub>8</sub> H <sub>16</sub> O <sub>5</sub>	64 at 0.25 mm. Hg	3	2.789	26.41	48.36	48.45
13	Trimethyl methyl- <i>d</i> -xyluloside	C <sub>9</sub> H <sub>18</sub> O <sub>5</sub>	52 at 0.25 mm. Hg	4	3.036	35.73	60.10	60.21
14	Dimethyl monoacetone <i>d</i> -xylu- lose	C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	47 at 0.1 mm. Hg	2	3.457	19.31	28.29	28.44
15	Dimethyl xylulose	C <sub>7</sub> H <sub>14</sub> O <sub>5</sub>	88 at 0.2 mm. Hg	2	3.292	22.20	34.55	34.84
16	Dimethyl methyl- <i>d</i> -xyluloside	C <sub>8</sub> H <sub>16</sub> O <sub>5</sub>	61 at 0.25 mm. Hg	3	2.955	27.93	48.27	48.45
17	5-Methyl monoacetone methyl- rhamnoside	C <sub>11</sub> H <sub>20</sub> O <sub>5</sub>	63 at 0.1 mm. Hg	2	3.480	17.92	26.62	26.72

TABLE III. DETERMINATION OF METHOXYL

No.	Compound	Formula	Boiling Point ° C.	Methoxyl Groups per Molecule	Weight	AgI <i>Mg.</i>	Meth- oxyl Found	Meth- oxyl Calcu- lated
					of Sample <i>Mg.</i>			
18	Trimethyl methyl- <i>d</i> -xyluloside	C <sub>9</sub> H <sub>18</sub> O <sub>5</sub>	52 at 0.25 mm. Hg	4	3.600	16.390	60.09	60.21
19	Dimethyl monoacetone xylulose	C <sub>10</sub> H <sub>18</sub> O <sub>5</sub>	47 at 0.1 mm. Hg	2	3.573	7.716	28.52	28.44
20	Dimethyl xylulose	C <sub>7</sub> H <sub>14</sub> O <sub>5</sub>	88 at 0.2 mm. Hg	2	4.184	10.950	34.57	34.84
21	Dimethyl methylxyluloside	C <sub>8</sub> H <sub>16</sub> O <sub>5</sub>	61 at 0.25 mm. Hg	3	3.308	15.933	48.15	48.45
22	Triacetylmethyl methylhexoside	C <sub>14</sub> H <sub>22</sub> O <sub>9</sub>	.....	2	4.775	6.685	18.48	18.55
23	Diacetyl dibenzoyl methyl- hexoside	C <sub>25</sub> H <sub>26</sub> O <sub>2</sub>	.....	1	5.875	2.831	6.36	6.38
24	α - Methyl - 2,3,4 - trimethyl - <i>d</i> - galacturonamide	C <sub>10</sub> H <sub>19</sub> O <sub>6</sub> N	.....	4	3.182	12.029	49.94	49.81
25	Dimethyl ester of 2,3,4-trimeth- oxy mucic acid	C <sub>11</sub> H <sub>20</sub> O <sub>8</sub>	.....	5	3.189	13.305	55.11	55.37



TABLE IV. DETERMINATION OF METHOXYL

No.	Compound	Formula	Methoxyl Groups per Molecule	Weight of Sample Mg.	Vol. of 0.02195 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Ml.	Methoxyl Found %	Methoxyl Calculated %
26	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	3.974	13.70	39.04	52.54
27	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	3.750	14.30	43.19	52.54
28	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	4.975	14.87	33.85	52.54
29	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	4.810	16.95	39.91	52.54
30	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	4.520	15.60	39.09	52.54
31	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	4.395	16.65	42.90	52.54
32	Hexamethylsorbitol	C <sub>12</sub> H <sub>26</sub> O <sub>6</sub>	6	4.480	20.80	52.70	69.87
33	Hexamethylsorbitol	C <sub>12</sub> H <sub>26</sub> O <sub>6</sub>	6	4.920	22.17	51.03	69.87
34	Hexamethylsorbitol	C <sub>12</sub> H <sub>26</sub> O <sub>6</sub>	6	4.170	21.50	58.39	69.87
0.01993 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>							
35	Trimethyl monoacetone glucose	C <sub>12</sub> H <sub>22</sub> O <sub>6</sub>	3	6.890	18.05	27.00	35.50
36	Trimethyl monoacetone glucose	C <sub>12</sub> H <sub>22</sub> O <sub>6</sub>	3	5.740	14.70	26.40	35.50

TABLE V. DETERMINATION OF METHOXYL

No.	Compound	Formula	Methoxyl Groups per Molecule	Weight of Sample Mg.	Vol. of 0.01064 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Ml.	Methoxyl Found %	Methoxyl Calculated %
37	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	3.348	32.06	52.70	52.54
38	Trimethyl methylglucoside	C <sub>10</sub> H <sub>20</sub> O <sub>6</sub>	4	2.902	27.70	52.53	52.54
39	Trimethyl monoacetone glucose	C <sub>12</sub> H <sub>22</sub> O <sub>6</sub>	3	2.882	18.63	35.58	35.50
40	Trimethyl monoacetone glucose	C <sub>12</sub> H <sub>22</sub> O <sub>6</sub>	3	2.822	18.17	35.44	35.50
41	Hexamethylsorbitol	C <sub>12</sub> H <sub>26</sub> O <sub>6</sub>	6	2.106	26.62	69.57	69.87
42	Tetramethylsorbitol	C <sub>10</sub> H <sub>22</sub> O <sub>6</sub>	4	2.618	25.02	52.60	52.03
43	Hexamethylmannitol	C <sub>12</sub> H <sub>26</sub> O <sub>6</sub>	6	2.028	25.74	69.85	69.87

ple. The safest procedure to follow, as found in this laboratory, is to add phenol and propionic anhydride, which are superior to phenol and acetic anhydride. The latter combination has been used in many instances with a longer period of boiling without giving correct analytical figures. The data in Table I substantiate the claim as to the efficacy of phenol and propionic anhydride.

Another important part of the author's procedure is to allow the reaction to proceed at room temperature, particularly when one or more of the alkoxyl radicals are in an ester form. Since the first product of the reaction will then be methanol, this might distill over, after the application of heat, without being converted into methyl iodide. The same condition obtains for volatile liquids; hence the advantage of having a condenser above the reaction flask. The expenditure of time for heating is well worth while, because it effects complete severance of the alkoxyl groups, irrespective of their number. Inasmuch as the procedure requires only occasional attention, the increase in time is not significant.

The disturbing occurrence of bumping so often discussed is best prevented by the use of a few Alundum grains.

When high methoxyl figures are anticipated it has been found necessary to have an excess of bromine in the absorbant, lest the alkyl iodide be incompletely oxidized, and the weight of the sample should be close to 3 mg., to ensure a sufficient excess of hydriodic acid.

According to Roth and Daw (15) the method using alcoholic silver nitrate as an absorbent is not applicable to sulfur-containing substances because the cadmium sulfate in the washer does not retain quantitatively the hydrogen sulfide liberated during the reaction. It has been the experience in this laboratory that by the addition of 1 or 2 crystals of iodine to the reaction mixture, the organically bound sulfur is oxidized practically quantitatively to the elementary form. Therefore, only a trace (if any) of hydrogen sulfide is formed, and this is easily retained by the cadmium sulfate. However, this is not a factor in the more generally employed volumetric method of Vieböck and Brecher (16).

A blank of 0.02 to 0.30 ml. has been found by Gibson and Caulfield (7) and Lieff, Marks, and Wright (10), depending on the purity of the reagents. If the best available chemicals are used the blank is negligible (16).

As shown in Tables I, II, and III, when the above described procedure is followed the results are equally accurate for

gravimetric or volumetric determinations, and for solids sirupy substances, and liquids with boiling points at, above or below that of the hydriodic acid. Duplicate analyses illustrate that the precision of the method is high. The data in Table IV were obtained independently (by J. A. Alicino, Department of Chemistry, Fordham University, New York, N. Y.) using the conventional procedure. The low figures (in some instances 10 to 15 per cent below the calculated value) and the inconsistencies for pure substances, which were checked by carbon and hydrogen determinations, are evident. Table V presents very satisfactory figures obtained (by Alicino) following the procedure now described (using information given in advance of publication by the present author).

The procedure and apparatus are the same for both methoxyl and ethoxyl groups.

### Acknowledgment

The author is greatly indebted to P. A. Levene for valuable suggestions.

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# THE NORTHEASTERN UNIVERSITY CHEMICAL LABORATORIES

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ON OCTOBER 3, 1938, the Chemical Laboratories of Northeastern University, located on the fourth floor of the new engineering building, were dedicated as the Hayden Memorial Laboratories, having been made possible by a gift from the Hayden Foundation. Coolidge, Shepley, Bulfinch & Abbott of Boston designed the building, which was constructed by the Sawyer Construction Company of the same city; the Kimball Company built and installed the laboratory furniture under the direction of Arthur B. Stanley.

The floor plan shows the interior arrangement of the laboratories. In addition, there are two storage vaults in the basement and a large lecture hall on the second floor which is shared with the physics department.

The walls, constructed of cinder block painted with buff casein paint, provide ample light reflection with no glare. The ceilings, which are pan type finished concrete painted the same color as the walls, have proved very effective in diffusing light and reducing reflected noise. The concrete floors are covered with asphalt tile in squares of dark red and black. This material resists common acids and alkalis in moderate concentration and the squares can be easily replaced if damaged. All laboratories and service rooms have steam, gas, electricity, and compressed air available, with outlets of a gun-metal oxidized copper finish. This finish gives a pleasing appearance and has been easy to keep clean.

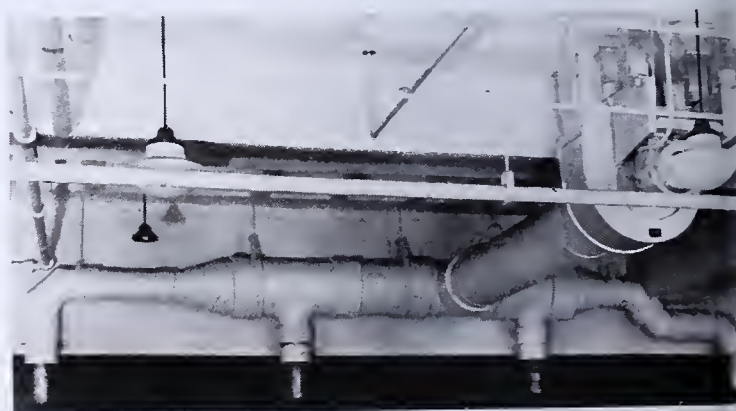
Every laboratory has a coat room and a conference room adjacent. The coat room has proved to be an excellent method of keeping the laboratory and halls neat, and the conference rooms are used continually.

Carl Muckenhoupt of the physics department designed the flexible electrical distribution panel. Varying direct current voltages from batteries can be distributed to circuits, as well as 115- to 120-volt direct current, supplied by the Boston Edison Company. Extra jacks are provided for future increase in the battery voltage and the layout is such that the batteries can be charged by either a Tungar or a generator.

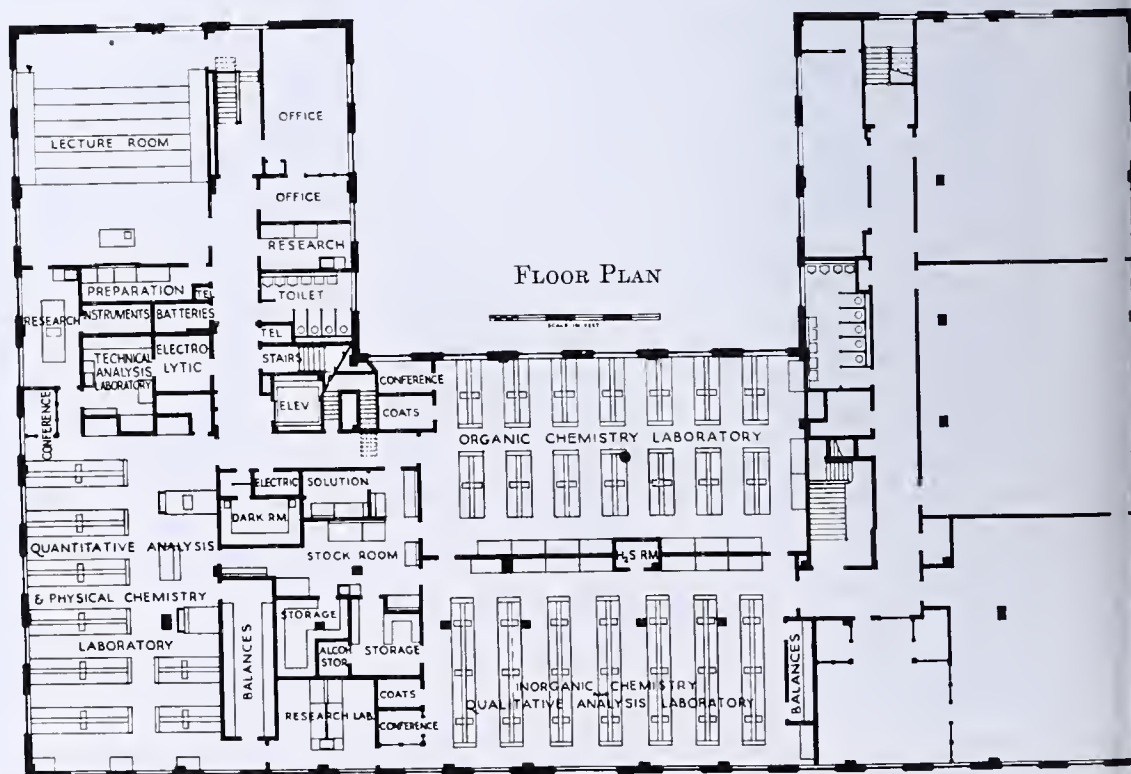
The distilled water tank is aluminum with a capacity of 100 gallons. The piping system is also aluminum, but the outlets in the laboratories are tin-lined self-closing bibcocks.

Fourteen exhaust fans for removal of fumes discharge into louvers in the roof. All fume ducts and piping are of noncorrosive Type S Transite pipe. The fan capacities vary between 300 and 2000 cubic feet per minute. No more than three ducts lead to one fan, and the fans are connected to the inlet pipe by asbestos acidproof cloth, which pre-

vents transmission of vibration from the fan. The dampers on the hoods are adjusted so that there is an intake of 40 feet per minute per square foot of hood opening. Louvers in the doors allow intake of air from the halls, so that no fumes escape from the laboratories. In the organic and inorganic chemistry and qualitative analysis laboratories unit heaters supply hot air removed by the hoods. These are automatically operated by thermostats for winter use; when heat is not on in the radiators, they can be operated manually for circulation of cold air. Each lecture room is on a separate ventilating system so adjusted that there is an exhaust of 15 cubic feet per minute per person if all seats are occupied. In addition, unit ventilators, which can be operated manually or by thermostat, recirculate room air over steam radiators until the thermostat temperature is reached, after which they draw fresh air from outside. They can also be adjusted to draw in outside air unheated when the outside temperature approaches room temperature.



TRANSITE DUCTS







*Top Left.* LABORATORY TABLES, SHOWING  
CERAMIC DRIP CUPS

*Top Right.* ORGANIC LABORATORY, SHOWING  
AISLE LAYOUT AND EMERGENCY SHOWER

*Center.* ORGANIC LABORATORY  
*Bottom.* INORGANIC LABORATORY



### Description of Laboratories

The general chemistry and qualitative analysis laboratory is 36 feet wide and 65 feet long and will accommodate 75 students at one time. It contains seven hoods, each 6 feet long, and seven laboratory tables, each 25 feet in length. The tables, placed 4 feet apart, contain three ceramic sinks each, and provide 756 locker spaces. A balance room opens off this laboratory and is equipped with triple-beam balances. A ventilated hydrogen sulfide room contains tank hydrogen sulfide and a gasometer. This gas is distributed through aluminum piping and hard-rubber cocks to the hoods.

The organic chemistry laboratory, 34 × 68.5 feet, contains fourteen laboratory tables each 12 feet in length; 56 students can comfortably work in the laboratory at one time. This room is also equipped with 112 sets of lockers, a wall type of glass-blowing table, seven hoods each 6 feet long, and a combination fume-hood and evaporator unit.

The quantitative analysis and physical chemistry laboratory is 34 feet long and 58 feet wide. There are six laboratory tables, 16.5 feet long; two tables, 11 feet long; one table, 6 feet long; and a physical chemistry table, 10.5 feet long, containing a constant-temperature bath with the accessories.

There are 120 lockers available and 50 students can work in the laboratory at one time. The hood system consists of three 4-foot hoods, two hoods 6 feet long, and a combination hood and evaporator unit 6 feet long. One hood contains an electrically heated sand bath. Connected with the laboratory is an insulated, well-lighted balance room, 9 × 27.5 feet, which will comfortably house 22 balances. An adjacent room 13 × 17 feet is equipped for technical analysis of industrial products. It contains four wall tables each 6 feet in length, a fume hood 6 feet long, and a large ceramic sink. Plenty of storage and drawer space is provided in the wall tables. The electrolytic room is used for such operations as electrometric titration and electrolytic analysis.

Three research laboratories are available; all are equipped with wall tables, fume hoods with outlets for gas, water, steam, and electricity, and accessories, such as constant-temperature baths, glass-blowing tables, and sinks.

A dark room, 14 × 17 feet, is equipped with working tables which are 3 feet 4 inches high and have a ceramic sink at each end. Ventilation is supplied by a lightproof fan. All the equipment necessary for copying work and for the preparation of lantern slides is available and there is space to set up optical apparatus.

The service rooms are designed to make a complete unit as far as possible. All the undergraduate laboratories are connected with the dispensing stock room, which adjoins the storage rooms for alcohol, chemicals, and glass apparatus. The solution room also connects with the main stock room and is a fully equipped laboratory, containing ample shelf room for maintaining a complete supply of chemicals and stock solutions. Rolling tables are used to transport solutions and chemicals from the solution room to the laboratory shelves. Two large and well-ventilated storage rooms in the basement contain the bulk of chemicals and other supplies, and a freight elevator is adjacent to these rooms and the main stock room. An internal telephone system and buzzers provide communication between the basement room, the main stock room, and the chemistry department office.

The lecture rooms on the fourth and second floors are each equipped with a preparation room containing wall tables, hoods, and steel storage cabinets. All materials necessary for lecture demonstrations are stored in these rooms, and demonstrations may be moved on rolling tables or passed into the room by raising the center blackboard section.

The lecture room on the fourth floor is 34 feet wide and 44 feet long and contains 150 seats in a sloping floor. The cen-

ter blackboard is one side of an illuminated hood in the preparation room and demonstrations requiring a hood may be set up and operated in this space. The lecture room table also contains a down-draft exhaust over which may be placed a fume hood of shatterproof glass, so that demonstrations performed in this hood are visible from all parts of the room.

### Laboratory Furniture

The fume hoods are of the open-front construction type, 33 inches wide. The working surface is Alberene stone and contains a ceramic waste drain with gooseneck faucets, steam, and gas. The electrical outlets are installed on the apron of the hood and there are two vaporproof lights in each hood operated by a switch located in the jamb. The hoods and adjustable baffles are made of Sheldine stone stained a light gray-green.

The area under the Alberene stone working surface is entirely enclosed with lead-clad steel and serves as a drying cabinet. This is well insulated to make working conditions at the hoods more comfortable; its two doors are made of two sheets of lead-clad steel with insulating material between them. The cabinet is vented into the ventilating system and the air is drawn in through screened holes located at the 4-inch toe-space of the hood. The source of heat is a closed steam radiator located at the floor and covered with a perforated Sheldine stone slab that forms the bottom of the cabinet. Two copper screens of different mesh support the apparatus to be dried.

The laboratory tables are 54 inches wide and vary in length from 12 to 25 feet. All are 37.5 inches high with Alberene stone working surface. Each table in the quantitative analysis, physical chemistry, and organic chemistry laboratories has one ceramic sink in the center into which ceramic troughs empty. The troughs are covered with removable stone covers pierced to take removable ceramic drip cups. There are gooseneck faucets at the sinks and stainless-steel steam cones on the organic chemistry desks. A false end is provided at the aisle end of each table to enclose the service pipes, so that the visible piping is kept to a minimum and at the same time shut-off valves are readily available.

The cabinet work is of selected Appalachian plain sawed white oak and the interior construction is of No. 1 common birch. The exterior panels are two-face plywood material matched for uniform figure and color.

The locks for the student lockers are combination padlocks with stainless-steel shell and electrochemically colored dial. The units, which contain two drawers and a cupboard, are arranged so that the drawers are fastened by a special catch operated from the cupboard, which allows one padlock to control the whole unit.

A large number of wall tables are used in the service rooms and the research laboratories. These tables are 33 inches wide and 37 inches high, and are equipped with the same services as the larger tables. The units consist of one locker and nine drawers of three different sizes.

The lecture tables are 12 feet long and 3 feet wide. In addition to the down draft previously mentioned they have all service connections similar to the laboratory tables.

The evaporator units are made of Alberene stone with three ceramic troughs, which have Monel metal covers and are supported on Alberene stone slabs. Each trough is 68 inches long, 7.5 inches wide, and 6 inches deep with a 4-inch standing removable waste and overflow, and has openings 3 inches square over each nest of rings, so that vapors can be drawn into the vent chamber. A slanted overhead glass plate with a gutter is located over each bath to lead away the condensate while the bottom of the vent chamber is drained by a heavily leaded drip pan.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Undissolved Sludge in Used Oils

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THE standard dictionaries—Webster's New International Dictionary, Hackh's Chemical Dictionary, and Van Nostrand's Scientific Encyclopedia—give a variety of definitions for sludge, but the common thought running through most of them is that sludge is a muddy or slimy deposit that settles or is deposited on sedimentation. This fits very well the undissolved sludge encountered in used oils.

TABLE I. INSOLUBLE MATTER IN FILTERED USED DIESEL ENGINE OILS

Solvent	Oil 1 <sup>a</sup> Mg./10 g.	Oil 2 <sup>a</sup> Mg./10 g.	Oil 3 <sup>a</sup> Mg./10 g.
Isopentane, C. P.	32	26	66
Pentane, commercial	31	21	62
n-Heptane	15	13	41
Isooctane, commercial	14	15	44
Precipitation naphtha	9	12	37

<sup>a</sup> Milligrams of precipitate per 10 grams of oil, the solvent to sample ratio being 10 to 1.

The sludge is muddy or slimy, instead of dry or solid, because it occludes oil. Since the amount of oil occluded continually decreases as the period of settling increases, it is impractical and of little significance to determine the mud or sludge accurately. Therefore the proposed method for the determination of undissolved sludge measures only the non-soluble component—that is, the characteristic constituent.

A knowledge of the amount of sludge which exists undissolved in samples of used, oxidized, or other unclarified motor oil is of special interest to the research worker who is concerned with the effect of refining processes and modifiers on the performance of lubricating oil, as well as with the impression the customer gets when he sees his drained crankcase oil.

The methods which are commonly applied for the determination of sludge are similar to those used to determine solubilities of bituminous materials. Among the solvents so employed are 86° (A. P. I. gravity) naphtha, A. S. T. M. precipitation naphtha, special light petroleum naphthas, and various pure hydrocarbons. The general procedure involves the hot or cold digestion of a weighed amount of sample with a measured amount of the particular solvent, followed by a period of settling, filtration through paper, asbestos, porous glass, or Alundum, washing with the solvent, drying, and weighing.

Such direct solubility methods are unreliable for determining undissolved sludge because the so-called solvent may

have a complex effect and not only dissolve the oil which is to be removed but also precipitate material which was actually in solution in the oil alone, the oil being commonly a better solvent than the analytical solvent employed in the analysis. Such a procedure measures not merely the undissolved sludge, but at best the sum of the undissolved plus an indeterminate amount of "dissolved sludge."

That ordinary paraffinic solvents may precipitate material which is in solution in the oil alone is illustrated by Table I. These data were obtained by filtering the undiluted used lubricating oil through cotton and running solubility tests on the filtrate with each of the solvents shown. Frequently the precipitable "dissolved sludge" is greater than the truly undissolved sludge (Table II), so that a true measure of the undissolved sludge is not reliably obtained by a simple solubility test on the used oil.

TABLE II. INSOLUBLE MATTER IN USED OILS

Oil Used in	C. P. Isopentane Solvent			Commercial Pentane Solvent		
	Unfiltered sample	Filtered <sup>a</sup> sample	Undissolved sludge	Unfiltered sample	Filtered <sup>a</sup> sample	Undissolved sludge
Mg. per 10 grams of oil						
Automobile	22	12	10	19	7	12
	315	133	182	284	100	184
	53	1	52	52	0	52
	47	1	46	44	1	43
Automobile truck	20	2	18	19	5	14
	25	7	18	29	6	23
	10	5	5	8	1	7
Automobile bus	238	19	219	230	16	214
1-Cylinder Diesel	34	4	30	32	3	29
CFR engine	334	15	319	327	10	317
6-Cylinder Diesel truck	581	59	522	580	49	531
Diesel	64	32	32	59	31	28
	82	10	72	82	11	71
	206	26	180	205	21	184
	59	6	53	56	4	52
	158	10	148	141	3	138

<sup>a</sup> Note that the insoluble matter in the filtered sample is occasionally greater than the undissolved sludge, so that a simple solubility test on the unfiltered sample is unsuitable as a means of determining undissolved sludge.

Furthermore, such solubility tests are influenced by the ratio of solvent to sample. There is an optimum solvent-to-sample ratio which yields the greatest amount of insoluble matter. It is commonly found that a large ratio will show a greater amount of undissolved matter in a particular sample than will a lower ratio, and this anomaly is explained by the fact that the amount of "dissolved sludge" precipitated by the solvent varies with the solvent-to-sample ratio.



### Details of Method

The method which the authors use comprises the determination of the pentane-insoluble matter in the sample and in the filtrate obtained by passing the undiluted sample through absorbent cotton. From the difference in the two values the undissolved sludge is calculated. This is the sludge undissolved by the oil itself; it does not include water, which may be separately determined. The method is theoretically sound and its laboratory manipulations are practical.

**SOLVENT.** Commercial pentane.

**APPARATUS.** The only special apparatus is a simple filter consisting of a glass tube, 508 mm. long  $\times$  17 mm. in inside diameter, containing a depth of 101 to 127 mm. of surgical absorbent cotton dry-packed at one end, a gauze cap supporting the cotton.

**PROCEDURE.** A representative portion of the sample is gravity-filtered through the cotton filter. This filtration is, for convenience, carried out overnight in a hot box at 65° to 75° C. On this clarified oil, as well as on a portion of the original sample, the matter insoluble in pentane is determined in the following manner:

Weigh 10 grams of sample into a suitable Erlenmeyer flask and to it add 100 ml. of pentane, agitating to maximum solution. Allow to stand stoppered overnight, then filter through well-packed asbestos in a Gooch crucible, using suction. Wash thoroughly with 100 ml. of pentane, suck dry, then heat in an oven at 110° C. for 1 hour and weigh.

**CALCULATION.** From the difference in the weights of insoluble matter the undissolved sludge is calculated as follows:

$$C = 1000 \left[ A - \left( B \frac{10 - A}{10 - B} \right) \right]$$

where  $A$  = sludge undissolved by pentane, original sample (grams per 10 grams)

$B$  = sludge undissolved by pentane, clarified sample (grams per 10 grams)

$C$  = undissolved sludge (mg. per 10 grams)

When  $A$  is low (0.1), for practical purposes  $C = 1000 (A - B)$ .

The authors have found it convenient to report results in mg. per 10 grams of sample.

This method gave results reproducible within 5 per cent on the sludge basis when the sludge content was high, but duplicate tests within 4 mg. per 10 grams are considered its limit of reproducibility. Used oils from a variety of crankcase services varied in undissolved sludge content from a few to hundreds of milligrams per 10 grams of sample.

This method of analysis includes undissolved mineral matter in the value for undissolved sludge. Determine the mineral matter separately in the usual manner by solution in mineral acids or by ignition.

The sludge, which may become visible on settling, will of course include water that is present. Therefore, when desired, the water should be determined on another portion of the sample, and for this the A. S. T. M. method (1) is suitable.

The proposed method is free of the faults of the other methods—namely, the error due to coprecipitation of matter which was dissolved in the oil sample itself, and the effect of solvent-to-sample ratio—because the solvent in identical ratio is applied to the filtered sample and the quantity of insoluble matter so obtained is used to correct the test made on the unfiltered sample. The quantity of insoluble matter obtained in the filtered sample is in itself unimportant; it merely serves as a correction for the similar material coprecipitated with the undissolved sludge in the original unfiltered sample. The ratio of solvent to sample is therefore unimportant, except that the same ratio must be used on the original unfiltered sample and on the cotton-filtered sample.

### Selection of Solvent

Of the common hydrocarbon series the paraffins are the poorest solvents for asphaltic and tarry matter, and the lower-boiling members are the poorest solvents of this series.

Since the undissolved sludge of a used oil may contain material of an asphaltic or tarry nature, besides carbon and mineral matter, the authors' efforts were concentrated on the pentanes. These are the lowest boiling liquid paraffin hydrocarbons that can be conveniently handled and experiments showed that they do not dissolve matter which exists undissolved in the used oil itself.

Much of the authors' original work had been done with c. p. isopentane because the use of this solvent was established practice at this laboratory for certain solubility tests. Subsequent work showed that results with commercial mixed pentanes checked those by isopentane. Since c. p. isopentane costs about five dollars and mixed pentanes less than one dollar per gallon, commercial pentane was adopted. Each has good solvent power for lubricating oil and neither dissolves sludge which is undissolved by the used oil itself. This latter point was shown by the fact that microscopical examination ( $\times 320$ ) of the pentane-soluble matter from a large number of used crankcase oils, taken at random, showed no black nor dark undissolved particles. The microscopical examination was made at room temperature after the evaporation of the solvent. The absence of dark particles proves that the pentane did not dissolve anything which the oil itself could not hold in solution. Any other solvent can be used, provided it dissolves the oil of the sample but not the undissolved sludge.

### Clarifying Used Oil

Various means were investigated for obtaining the clarified sample.

The filtering medium must be inert; hence active clays, etc. are to be avoided. A 15-cm. (6-inch) layer of sand was inadequate, permitting the passage of the fine sludge of used crankcase oils. A 5-cm. (2-inch) layer of Filter-Cel was too dense, requiring weeks for the recovery of a few grams of filtrate. A 10-cm. (4-inch) layer of sand over a 5-cm. (2-inch) layer of Filter-Cel was unsuitable for the same reason as the Filter-Cel alone. Filtration through filter paper (Whatman's No. 44) was unsatisfactory; a single paper allowed the sludge to pass through; three papers clarified the oil, but filtration required days and often weeks as creeping caused trouble. Absorbent cotton was the best filtering medium found, yielding a clear filtrate in a reasonable time. At these filtrations were of the gravity type.

Attempts at reduced-pressure filtration were unsuccessful, the fine sludge of the samples soon came through the filter clogged it completely. Centrifuging the undiluted sample 75° C. for 4 hours at 6000 r. p. m. was also tried, but it did not ensure complete sludge removal as judged by the appearance of the spot made on filter paper by a drop of the centrifuged oil.

TABLE III. UNDISSOLVED SLUDGE IN USED OILS

Clarification Procedure	Motor Oil	Airplane Oil		Diesel Lubricating Oil
		1	2	
		<i>Mg. per 10 grams</i>		
Centrifuging	3	63	59	57
Filtration through cotton	5	62	56	56

For the authors' purpose it is necessary that the filtering medium, used to obtain the clarified sample, be one which neither reacts with nor selectively adsorbs material components of the sample being filtered through it. That absorbent cotton is such an inert filtering medium was shown by the fact that results obtained with its use satisfactory compared with checked results obtained using clarified oil which was prepared by prolonged high-speed high-temperature (70° C.) centrifuging without the use of any filtration medium. A comparison of typical results obtained with oils clarified by cotton and by centrifuging is given in Table III.

Some viscous oils which contain large amounts of undissolved sludge do not yield as much as 10 grams of filtrate through cotton overnight. Such samples should first be centrifuged to remove the bulk of sludge and then filtered through cotton in the usual manner.



Microscopic examination ( $\times 320$ ) at room temperature of the "filtrates through cotton at 65° to 75° C." from numerous used crankcase oils, taken at random, showed no dark particles in most of them; a small percentage showed a few isolated particles estimated to be not more than 2 per cent of the amount visible in the samples before the filtration. The absence of the dark particles proves that the oils while filtering at the elevated temperature did not dissolve sludge which they could not retain in solution at room temperature. Since crankcase oils in use are commonly at these and even higher temperatures and hence have the opportunity to act on the sludge, the additional warm period during filtration should not materially influence the solution of the sludge in the oil.

Attempts at determining undissolved sludge by filtering the undiluted sample through a weighed filter, followed by wash-

ing the residue on the filter with a suitable solvent, failed completely. The fine sludge of the sample soon came through the filter or clogged it completely.

### Acknowledgment

The authors acknowledge their appreciation of the assistance of A. J. Millendorf, S. K. Williams, and F. P. Farrell, who did most of the analytical work. They also wish to acknowledge the unpublished contributions of C. G. Ludeman of this laboratory on this general subject.

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# Determination of Dissolved Sludge in Used Oils

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IN THE present terminology of the petroleum industry the word "sludge," when considered in connection with used oils, usually refers to material thrown out of oil by the chemical and physical changes resulting from use in an engine. Some definitions include the mineral and metallic particles resulting from wear, abrasion, and contamination, while others particularly exclude these inorganic products and include only insoluble materials of hydrocarbon origin. However, most neglect those other degradation, polymerization, or oxidation products which may be dissolved in the used oil, but which may properly be considered dissolved sludge, since they are not present in the original oil but are formed during use. Such dissolved materials are probably an indication of what may come out of solution on further use or dilution and contribute to lacquer- or gumlike deposits on engine parts. As separated in the proposed method, the dissolved sludge precipitates in forms varying from finely divided particles almost microscopic in size to large agglutinated particles, but in all cases on evaporation from benzene solution it is obtained as a lustrous, brittle, continuous, adherent lacquerlike film, varying from pale yellow to dark red-brown in color—very similar to lacquerlike engine deposits.

TABLE I. EFFECT OF PROPANE DESLUDGING TEMPERATURE ON SLUDGE VALUES OF USED OILS

Desludging temperature, ° C.	22	66
Dissolved sludge, mg. per 10 grams	30	31
	148	167
	148	185
	157	177
	640	750

Using the method for the determination of undissolved sludge previously presented (1) and the method for determining dissolved sludge described here, the quantity and distribution of sludge present in used motor oils can be determined.

To arrive at a measure of the dissolved sludge, the material soluble in propane is determined on the clarified sample obtained by passing it undiluted through a filter tube packed with cotton (1). The determination is carried out at room temperature. Employing liquid propane at higher temperatures commonly gives larger quantities of insoluble material (Table I), but since well-made lubricating oils may have

components which are insoluble in hot liquid propane, calling such matter sludge is unjustified. On the other hand, that which is thrown out by liquid propane at ordinary temperatures is asphaltic, generally absent from well-made motor oils, and considered undesirable.

The amount of insoluble matter found in an oil commonly increases as the boiling point of the paraffin hydrocarbon used as a solvent decreases. Though more insoluble matter may be found by using liquid ethane or methane than by using propane, their low critical temperatures would greatly complicate the apparatus and method and the same objection would apply as to the use of hot propane.

Classifying as dissolved sludge only that portion (of a clarified used motor oil) which is insoluble in liquid propane is obviously empirical. However, it has been found useful in the study of motor oils to know not only the undissolved sludge which may be visually observed and is objectionable from the customer's point of view, but also the dissolved sludge which may be just as objectionable from the engineer's standpoint, since it represents alteration products of the oil and may be considered as potential sludge.

On residual oils it is desirable to determine the dissolved sludge on the unused oil also, in order to evaluate better the change brought about by service or engine tests.

### Method

The following method has been in use in this laboratory for several years:

The sample is clarified by filtration, undiluted, through absorbent cotton, using the apparatus previously described (1).

**APPARATUS.** The desludging apparatus is shown in Figures 1 and 2. It consists of a  $184 \pm 1$  mm. section of Pyrex "high-pressure" gage glass tubing 32 mm. ( $+0.5$  to  $-1.5$  mm.) in outside diameter with a wall thickness of approximately 3 mm., having one end sealed, closed, and rounded to a radius of approximately 16 mm., and the open end fire-polished flat at right angles to the axis of the cylinder. The tubes were made on order by the Corning Glass Works.

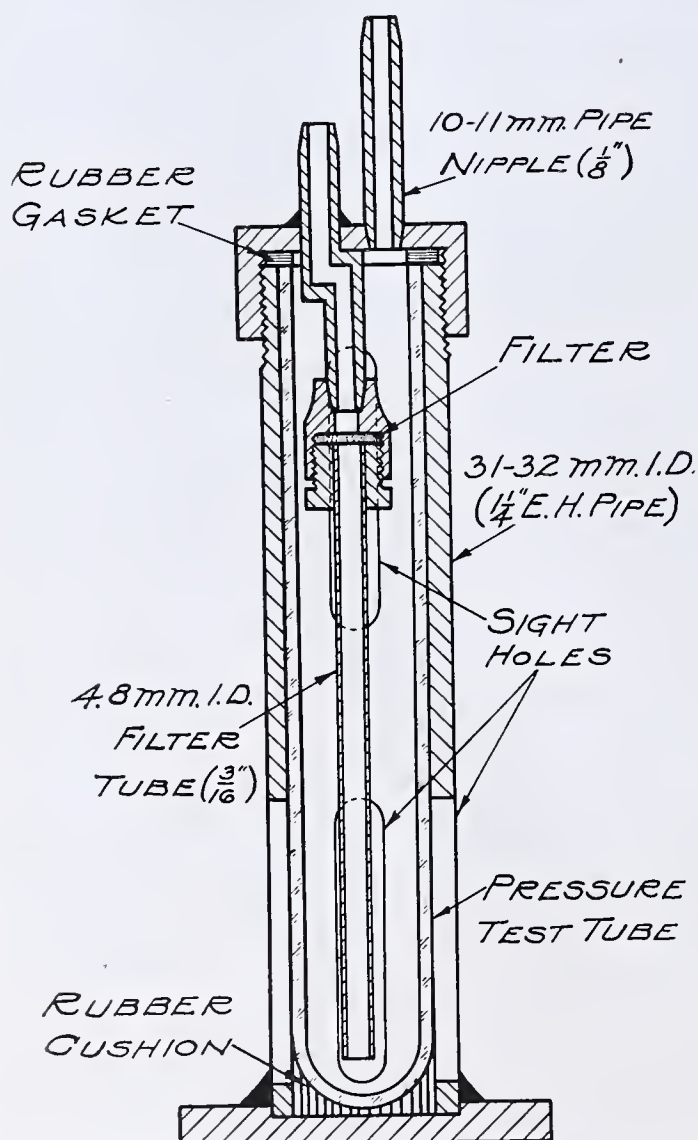
The pressure assembly for the test tube is shown in Figures 1 and 2. The outside tube is made of seamless brass tubing and should fit the glass tube snugly. The rubber cushion is made from a rubber stopper of good grade, hollowed to fit the bottom of the tube.



FIGURE 1. LABORATORY PROPANE DESLUDGING APPARATUS



FIGURE 2. SECTIONAL ELEVATION OF DESLUDGING APPARATUS



As a safety precaution a reinforced glass shield should be used around the pressure assembly, as shown in Figure 3.

**PROCEDURE.** The filter which must be placed in the filter cap (Figure 2) is made by cutting a disk from blotter press paper with the aid of a cork borer of the proper size. A suitable paper is the Eaton and Dikeman Co.'s filter paper No. 625 (0.66 mm., 0.026 inch). This disk serves both as filter and gasket. To prevent a large sludge from clogging this filter, the tube is packed with absorbent cotton from the filter downward for a distance of about 76 mm.

Four grams of the clear sample are weighed into the pressure test tube and the apparatus is assembled. The metal cap, with valves 1 and 2 closed (Figure 3), is screwed on hand-tight, finishing by holding the cap in a vise. During assembly, the apparatus should be held in an inclined position so as to keep the sample from rising to the filter, valve 1 being kept closed for the same reason and valve 2 being closed to protect the gage.

The assembly is now rotated in an inclined position so as to distribute the sample over a large surface and is then placed in the wired glass frame. For safety, stout goggles should be worn when working with propane in this test, since at room temperature the pressure within the test tube is of the order of 10.5 kg. per sq. cm. (150 pounds per square inch). Liquid propane (commercial, 98 per cent purity, free from odorants and nonhydrocarbon substances, has been used for all tests) from an inverted cylinder is introduced through valve 1, valve 3 being left open for a few moments to allow air to be displaced. Valve 3 is now closed, the apparatus set upright, valve 2 opened, and the introduction of liquid propane continued until the liquid level is at the mark on the pressure test tube. By means of a sticker the test tube is marked at a level so that the liquid volume assembled will be 6 ml. Valve 1 is closed and the adjacent union disconnected from the propane supply. Valve 2 is closed to protect the gage and the entire assembly (Figure 3) gently agitated until all the liquid dissolves. The assembly is returned to an upright position and allowed to remain that way for 20 minutes or until the sludge has settled, valve 2 being opened each time the assembly is let in an upright position.

A short length of copper tubing is connected to the nipple of valve 1 and the propane solution pressure-decanted through valve 1, which is opened slightly so as to maintain the pressure on the liquid substantially beyond the discharge end of the valve.

The sediment is washed by refilling the test tube with propane in a similar manner but this time the propane is introduced



through valve 3, though pressure-decanted through valve 1. The washing is similarly repeated twice more.

Care should at all times be taken to vent the propane slowly, so as to avoid chilling the apparatus. When the pressure is down to atmospheric the apparatus is dismantled and the sediment is dissolved by means of warm benzene from the test tube, filters, gasket, and other parts where it could have been deposited during the test. The benzene solution is then filtered through a rapid paper (Whatman's No. 41 H, 9 cm.) into a small tared beaker, the filtrate is evaporated on a steam bath, and the residue is dried in an oven at 110° C. and weighed.

The weight of dissolved sludge multiplied by the decimal fraction of "dissolved sludge plus oil" in the sample gives the dissolved sludge on the basis of the original unfiltered sample.

Dissolved sludge is reported in terms of milligrams per 10 grams.

Experimental

Results obtained on used oils have shown that frequently the dissolved sludge is greater than the undissolved. Typical results are shown in Table II.

TABLE II. TYPICAL VALUES FOR DISSOLVED AND UNDISSOLVED SLUDGE

Sample	Used Motor Oil	Dissolved Sludge <sup>a</sup>	Undissolved Sludge
		Mg./10 g.	Mg./10 g.
1	From laboratory test car	151	112
2	From road test car A	17	9
3	From road test car B	7	2
4	From road test car C	36	45
5	From road test car D	20	28
6	From Diesel truck E	67	392
7	From Diesel truck F	42	391
8	Used airplane oil, from laboratory test engine	153	7

<sup>a</sup> Note that dissolved sludge is frequently greater than undissolved.

The method has yielded results reproducible within 5 per cent on samples containing large amounts of dissolved sludge, and within 5 mg. per 10 grams on samples containing small amounts.

For work with hot propane, the authors employed a brass assembly similar to Figure 1 except that the brass bomb had no sight holes, the pressure test tube was not used, a higher pressure gage was used, and a transfer case was employed to introduce the propane. Hot propane was not deemed desirable for dissolved sludge determinations.

TABLE III. EFFECT OF RATIO OF SOLVENT TO SAMPLE ON SLUDGE VALUES OF USED OIL

Ratio of Solvent to Sample	Dissolved Sludge				
	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5 <sup>a</sup>
		Mg. per 10 grams of oil			
30:1	100	134	156	20	2180
15:1	152	153	150	34	2300
10:1	141	158	134	18	2330
7:1	136	136	110	..	2260

<sup>a</sup> Samples 1 to 4 were used engine oils; sample 5 was a white medicinal oil after oxidation at 171.7° C. (341° F.) under conditions of the German tar-forming number test. Desludging with propane was done at room temperature (22° C.).

This work has also shown that the amount of dissolved sludge thrown out by propane varies on some samples with the solvent-to-sample ratio (Table III) and the maximum

sludge precipitated does not occur at a uniform ratio for different samples. The ratio which has been adopted was selected as being of most general utility and it is hoped that the method will find use as a tool in the complicated task of used oil analysis.

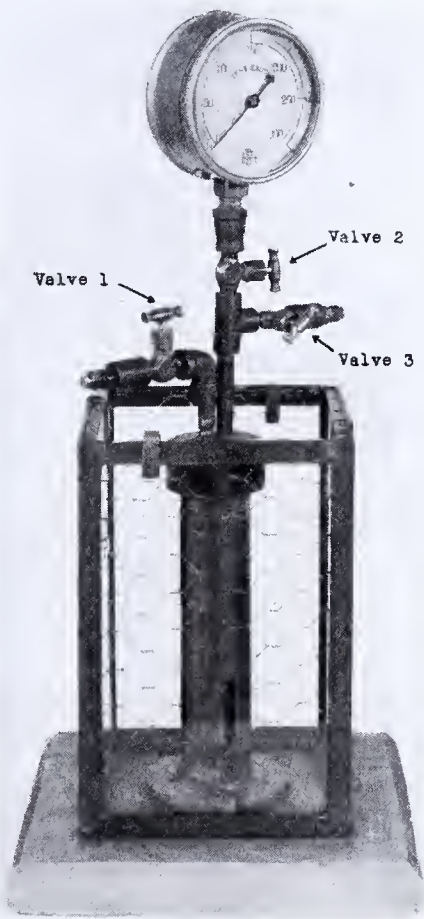


FIGURE 3. DESLUDGING APPARATUS ASSEMBLED

Unsatisfactory results are obtained when one attempts to determine undissolved sludge by means of propane tests on the original and filtered samples of a used oil. This is due to the fact that fine hard particles of the original sample are forced through the filter in the pressure decantations and small particles of dirt or bearing metal constitute a large proportion of the sludge.

Acknowledgment

The authors wish to acknowledge the assistance of J. R. McDowell, H. C. Becker, and A. J. Millendorf, who did most of the analytical work involved in the development of this method.

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# Tetraphenylarsonium Chloride as an Analytical Reagent

## Titration by Iodine

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**M**ETHODS in which tetraphenylarsonium chloride may be used as an analytical reagent for mercury, tin, cadmium, zinc, and perrhenate have been developed by the authors and will be described in subsequent papers. Lamprey (3), who did the exploratory research in connection with the reagent, showed that it could be used for the determination of perchlorate, periodate, gold, and platinum, but his studies were not exhaustive. He showed that the reagent could be used gravimetrically, or volumetrically by titrating the excess of standard reagent potentiometrically with iodine.

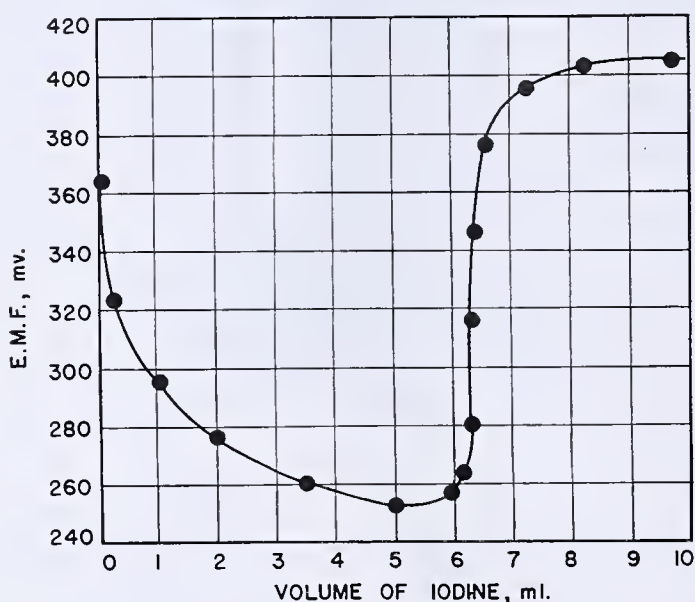


FIGURE 1. TETRAPHENYLARSONIUM CHLORIDE TITRATED WITH IODINE  
Solution saturated with sodium chloride

Tetraphenylarsonium chloride (obtainable from Merck & Co.) was prepared according to the method of Blicke and Marzano (1), with slight modifications developed by the authors and others. According to Blicke and Monroe (2) the aqueous solution is a strong electrolyte which yields tetraphenylarsonium,  $(C_6H_5)_4As^+$ , and chloride ions.

Three types of reactions have been noted in which the reagent is serviceable:

1. The formation of insoluble salts by the combination of the tetraphenylarsonium ion with such ions as perrhenate, permanganate, periodate, and perchlorate. Such determinations were most conveniently made gravimetrically.
2. The formation of insoluble compounds by the combination of the tetraphenylarsonium ion and the complex mercuric, stannic, cadmium, and zinc chloride ions. Such determinations were made by titrating the excess of standard tetraphenylarsonium chloride potentiometrically with iodine.
3. The formation of insoluble compounds with such thiocyanate complexes as those of iron and cobalt. These reactions have not yet been thoroughly investigated, but they appear to present analytical possibilities.

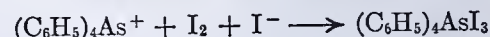
The analytical behavior of several other arsonium ions was studied. Although all gave precipitates resembling those ob-

tained with tetraphenylarsonium ion, none reacted quantitatively with iodine or with perchlorate, perrhenate, or chlorocadmiate ions. The compounds were similar to tetraphenylarsonium chloride with one of the phenyl groups replaced by an alkyl or substituted alkyl group. The compounds tried were iodomethyltriphenylarsonium chloride, triphenylarsinehydroxy chloride, phenacyltriphenylarsonium chloride, allyltriphenylarsonium bromide,  $\beta$ -hydroxyethyltriphenylarsonium chloride, methyltriphenylarsonium chloride, and carboxymethyltriphenylarsonium chloride. The effect of the substitution of an alkyl group for the phenyl group is to increase the solubility of the compounds.

Since the determinations of the mercuric, stannic, cadmium, and zinc ions depend upon the potentiometric titration of the excess of standard tetraphenylarsonium chloride by means of standard iodine solution, this titration is discussed in this paper. Applications of the reagent will be presented in subsequent papers.

### Potentiometric Titration of Tetraphenylarsonium Chloride with Iodine

This titration, by means of which the tetraphenylarsonium chloride solution is standardized, depends upon the reaction



and the fact that there is a sudden large increase in the oxidation potential when an equivalent quantity of iodine containing iodide has been added to the tetraphenylarsonium chloride solution (Figure 1). It is seen from the equation that one molecular weight of tetraphenylarsonium chloride requires two atomic weights of iodine and one of iodide.

TABLE I. GRAVIMETRIC DETERMINATION OF TETRAPHENYLARSONIUM ION

[5 ml. of $(C_6H_5)_4AsCl$ in 100 ml. of saturated NaCl solution]		
$I_2$ Used	$(C_6H_5)_4AsI_3$ Calcd.	$(C_6H_5)_4AsI_3$ Found
Mg.	Mg.	Mg.
13.83	41.6	41.8
13.83	41.6	41.6
13.80	41.5	41.7
13.87	41.7	41.8
13.83	41.6	41.6

The reaction is carried out in volumes less than 150 ml. in saturated sodium chloride solution. Since the product, a rusty-orange precipitate, does not form unless the iodine solution contains potassium iodide, it is evident that the reaction consists of the union of the tetraphenylarsonium and periodide ions rather than the union of tetraphenylarsonium chloride and iodine, as had originally been supposed. This is indicated by the data of Table I, secured by weighing the precipitates obtained from several potentiometric titrations. Measured volumes of standard tetraphenylarsonium chloride solution were titrated potentiometrically with standard iodine solution. The precipitates were filtered through Gooch crucibles, washed with water, dried at  $105^\circ C.$ , and weighed. Within the limits of experimental error the observed weights of the precipitates are the same as the weights of tetraphenylarsonium periodide calculated from the volume of standard

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iodine used. However, the gravimetric standardization of the reagent with excess iodine is not as convenient nor as precise as the potentiometric method.

The potentiometric standardization is carried out as follows:

Five to 10 ml. of the aqueous tetraphenylarsonium solution, 0.01 to 0.03 *M*, are measured and diluted to nearly 100 ml. with water or saturated sodium chloride solution. The reference and indicator electrodes are immersed in this solution while standard iodine solution of about the same concentration, containing 6 to 8 grams of potassium iodide per liter, is added slowly with constant stirring. As the iodine is added the potential of the system steadily decreases to a minimum value. When this minimum is reached, the iodine is added dropwise and time allowed for the system to reach equilibrium. When an equivalent quantity of iodine has been added there is a sudden increase in potential amounting to 25 to 35 millivolts per 0.01 ml. of 0.02 *N* iodine. Near the end point the solution must be completely saturated with salt before the titration is completed.

Any type of potentiometer system may be used. The indicator electrode was a smooth platinum wire and the reference electrode a calomel half-cell.

By the above procedure 4 to 100 mg. of tetraphenylarsonium chloride can be determined conveniently, and successive titrations duplicated within 0.02 to 0.03 ml. of 0.02 *N* iodine solution. The optimum concentration is 10 to 50 mg. of the reagent in about 100 ml. of solution, although acceptable results are obtained in 200 ml. It is best to saturate with sodium chloride just before the end point is reached. The time required is 20 to 30 minutes.

TABLE II. EFFECT OF SODIUM CHLORIDE CONCENTRATION ON TITRATION

[1 ml. of reagent solution contains 4.086 mg. of (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl]		
NaCl Moles/l.	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl Ml.	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl Mg./ml.
0	20	4.10
0	10	4.12
0	5	4.18
0	1	4.39
1.00	5	4.14
2.50	5	4.11
4.00	5	4.084
4.50	5	4.090
5.00	20	4.080
5.00	10	4.080
5.00	5	4.082
5.00	2	4.087

For best results the temperature of the solution being titrated should be 20° to 30° C., and never above 40° to 45° C., because of the volatility of the iodine and the increased solubility of the periodide precipitate.

TABLE III. SOLUBILITY OF TETRAPHENYLARSONIUM CHLORIDE IN AQUEOUS SODIUM CHLORIDE SOLUTIONS

(60-Ml. volume. Temperature, 30° C.)		
NaCl Moles/l.	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl G./100 ml.	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl Mole/l.
0	32.50	0.776
1.0	10.43	0.240
2.0	1.27	0.038
2.5	0.459	0.011
3.0	0.205	0.0049
3.5	0.101	0.0024
4.5	0.034	0.00081
Satd.	0.011	0.00026

The influence of the sodium chloride concentration is shown by Table II. Equilibrium is attained very slowly in low salt concentrations, thus making the titration very slow and uncertain. However, when the solution is almost saturated with sodium chloride, equilibrium is reached in a short time, and constant and easily reproducible results are obtained. A small amount of potassium iodide produces similar results but may form insoluble tetraphenylarsonium iodide. Although the tetraphenylarsonium chloride precipitates slowly, it is insoluble in concentrated sodium chloride solution, as Table III shows. Since the conversion of solid

tetraphenylarsonium chloride to the periodide is very slow, it is best to avoid formation of the solid by beginning the titration with a moderate salt concentration and completing the saturation just before the end point is reached. The standard iodine solution should not contain more than 6 to 8 grams of potassium iodide per liter of 0.01 to 0.02 *N* solution; otherwise insoluble tetraphenylarsonium iodide will form.

The solubilities in water of other tetraphenylarsonium halides at 25° C. were investigated, and are presented in Table IV.

TABLE IV. SOLUBILITIES OF TETRAPHENYLARSONIUM HALIDES (Temperature, 25° C.) \*

Compound	Solubility	
	G./100 ml.	Mole/l.
Tetraphenylarsonium fluoride	17.45	0.434
Tetraphenylarsonium chloride (30° C.)	32.50	0.776
Tetraphenylarsonium bromide	1.29	0.0279
Tetraphenylarsonium iodide	0.14	0.0028

A typical titration curve is shown in Figure 1. The first portion of the curve, in which the potential falls rather sharply as the iodine is added, probably corresponds to the removal of tetraphenylarsonium ion. The potential rises abruptly with the first slight excess of iodine, and the addition of a further excess causes a negligible change.

The direct titration of the reagent with iodine, or the titration of the excess of iodine with standard thiosulfate in the presence of the periodide precipitate with starch as the indicator is impossible, since the color of the precipitate obscures the color of the starch-iodide complex. The potentiometric titration of excess iodine with thiosulfate in the presence of the precipitate is impossible because of the uncertainty of the end point.

TABLE V. EFFECT OF ACIDITY AND NITRATES ON TITRATION

[5 ml. of (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> AsCl in 100 ml. of solution saturated with salt]		
Iodine Required Ml.	Substances Present besides Sodium Chloride	
4.58	None	
4.58	Concd. HCl, 2.0 ml.	
4.56	Concd. HCl, 3.0 ml.	
4.57	NaNO <sub>3</sub> (neutral), 2.0 grams	
4.58	NaNO <sub>3</sub> , 2.0 grams	
	Concd. HCl, 0.2 ml.	
4.58	NaNO <sub>3</sub> (neutral), 10.0 grams	
	80% salt satn.	
4.50	NaNO <sub>3</sub> , 10.0 grams	
	Concd. HCl, 1.0 ml.	
	80% salt satn.	
4.35	NaNO <sub>3</sub> , 10.0 grams	
	Concd. HCl, 1.0 ml.	
	80% salt satn.	
	More time allowed than in preceding titration	

The presence of free acid, except nitric acid, in moderate amounts is not objectionable, as shown by Table V. Nitric acid, and nitrates in the presence of acid, oxidize the iodide in the standard iodine solution to free iodine, causing the end point to be premature. When nitrates are present, the solution is neutralized to methyl red with sodium bicarbonate before titrating. Large quantities of nitrate cause the precipitation of tetraphenylarsonium nitrate.

Other chlorides, except those capable of oxidizing iodide or reducing iodine and those that form complex halide ions, may be substituted for sodium chloride. Other salts, such as sulfates, are not as effective in coagulating the precipitate. The alkalis and alkaline earths, nickel, cobalt (ous), chromium, manganese, borate, bicarbonate, acetate, phosphate, sulfate, citrate, and tartrate even in fairly high concentration do not interfere. The solution must be neutral or slightly acid. All anions that form fairly insoluble compounds with the reagent—e. g., tungstate, molybdate, chromate, perrhenate, permanganate, periodate, perchlorate, iodide (except in the iodine solution), bromide and fluoride—and all cations that form complex halide ions—e. g., zinc, cadmium, mercuric,



thallic, stannic, bismuth, ferric, platinum, and auric—interfere.

Ferrous ion (100 mg. or less) may be present. When ferric ion is present the addition of about 2 ml. of sirupy phosphoric acid and 2 grams of disodium phosphate will eliminate interference up to 200 mg. of iron, but results are not ideal with

TABLE VI. EFFECT OF CERTAIN CATIONS ON TITRATION

[5 ml. of  $(C_6H_5)_4AsCl$  in 100 ml. of solution saturated with sodium chloride. 5 ml. of  $(C_6H_5)_4AsCl$  are equivalent to 7.17 ml. of iodine solution]

Iodine Required Ml.	Substances Present besides Sodium Chloride
7.18	$MnCl_2 \cdot 2H_2O$ , 1 gram
7.17	$CrCl_3 \cdot 6H_2O$ , 1 gram
7.17	Sodium citrate, 8.8 grams
7.23	Sodium citrate, 17.5 grams
7.17	$Cu^{++}$ , 400 mg.
	Sodium citrate, 4 grams
7.16	$Cd^{++}$ , 88 mg.
	Sodium citrate, 4.5 grams
7.20	$Zn^{++}$ , 10 mg.
	Sodium citrate, 4.5 grams
7.28	$Bj^{+++}$ , 33 mg.
	Sodium citrate, 4.5 grams
7.33	$Sn^{++++}$ , 16 mg.
	Sodium citrate, 4.5 grams
7.16	$Fe^{+++}$ , 200 mg.
	Disodium phosphate, 2 grams
7.22	$FeSO_4 \cdot 7H_2O$ , 500 mg.

amounts beyond 100 mg. Citrate and tartrate are not effective in this respect, but citrate prevents interference by rather large amounts of cupric ion and by very small amounts (a very few milligrams) of tin, bismuth, zinc, and cadmium. A few grams of sodium citrate and enough citric acid to make the solution acid to methyl red are added before titrating. Table VI shows the effect of various cations on the titration.

All common organic solvents interfere either by preventing precipitation or by obscuring the end point.

### Summary

Tetraphenylarsonium chloride is useful as a reagent for determining mercuric, stannic, cadmium, zinc, perrhenate, periodate, perchlorate, and other ions.

Periodate, perchlorate, permanganate, perrhenate, fluoride, bromide, iodide, thiocyanate, molybdate, chromate, tungstate, and large amounts of nitrate interfere by forming insoluble salts with the reagent.

Mercury, tin, cadmium, zinc, platinum, gold, bismuth, and iron, the complex halide ions of which form insoluble compounds with the reagent, and all ions that can oxidize iodide or reduce iodine interfere.

Interference by copper, iron, cadmium, zinc, bismuth, and tin may be eliminated to some extent.

The reagent may be standardized potentiometrically with standard iodine, the reaction producing a rusty-orange precipitate of tetraphenylarsonium periodide.

The total volume to be titrated should be about 100 ml. of neutral or slightly acid solution saturated with sodium chloride just before the end point is reached.

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FROM a thesis presented by G. M. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

## Duplicating Pipets

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PIPETTS similar to Ostwald-Van Slyke "between marks" pipets, but having two bulbs, offer many advantages.

1. The amount of solution required to fill the uncalibrated part of the pipet below the lower mark is half as great for the two samples as for samples taken in two fillings of a single-bulb pipet. This small saving of the specimen is often important where a number of different analyses are required on a limited sample of blood or serum or where capillary blood samples are used. Pipet A, Figure 1, has been used where economy of sample is important—for instance, routinely in taking samples of serum or plasma for cholesterol determinations by the author's method.

2. When duplicate samples of a supernatant solution are to be drawn off from above a precipitate which is easily disturbed, the use of the duplicating pipet avoids stirring up this precipitate between samples. Pipet B has been used for taking samples of supernatant fluid for ascorbic acid determinations after precipitation of proteins. Its greater length of tip is convenient in removing samples from or delivering to narrow tubes, etc.

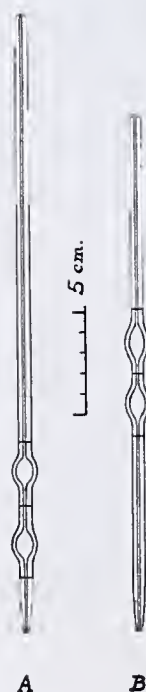


FIGURE 1.  
DUPLICATING PIPETS

3. Whenever it is undesirable to use the same single bulb pipet for a second sample—for example, in avoiding exposure of a thin film of sample to air on the walls of the pipet or the trapping of persistent bubbles in a viscous solution—the use of a single duplicating pipet in place of two single pipets effects a saving in cost of pipets, and in time consumed in washing the pipets.

4. Even though a single pipet could be used, the duplicating pipet saves the analyst's time, and, what is more important, speeds up the handling of unstable solutions.

5. The average of duplicates involves errors at only two calibration marks instead of four.

Specifications are purposely omitted from Figure 1, since these are type forms which can be modified to adapt them to particular uses.

FROM The Children's Hospital Research Foundation and the Department of Pediatrics, College of Medicine, University of Cincinnati.

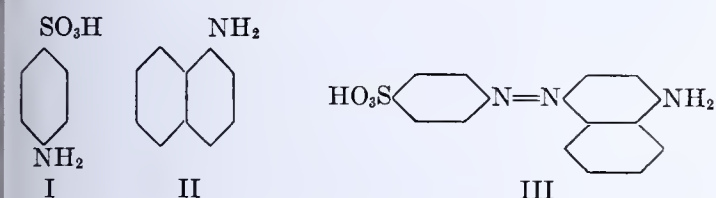


# Spectrophotometric Determination of Nitrite

## And of Nitric Oxide in Furnace Atmospheres

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GRIESS (6) first discovered that nitrous acid could be detected by reacting it with sulfanilic acid (I), coupling the resulting diazonium compound with  $\alpha$ -naphthylamine (II) to form a highly absorbing pink azo dye (III):



Perhaps the most sensitive method of detecting nitrite or nitrous acid as such (5, 7, 8), the formation of this dye can also be used to measure amounts of any substance that will yield nitrite in known proportion—for example, traces of oxygen could be determined by the use of nitric oxide in large excess. Over a year ago, the problem of estimating the small amounts of nitric oxide in certain furnace atmospheres arose in this laboratory, and the authors were led to investigate the usefulness of Griess's reagent for this purpose. Recently they discovered that Bennett (2) had already completed a similar investigation, employing visual methods where they used a recording spectrophotometer (15), and that their results in general confirm his earlier findings.

Griess's reagent, as modified by Ilvossay and Lunge, was prepared approximately according to the directions of Denis (4).

Sulfanilic acid (0.5 gram) was dissolved in 150 cc. of 5 *N* acetic acid; 0.1 gram of  $\alpha$ -naphthylamine was boiled with 20 cc. of water, filtered while hot, and the filtrate added to 150 cc. of 5 *N* acetic acid. The two solutions were mixed and kept in a glass-stoppered bottle that stood in the dark. A known aqueous potassium nitrite solution containing 10 micrograms per cc. was prepared from the c. p. salt (84.5 per cent  $\text{KNO}_2$ ). Standard nitrite solutions for colorimetric work were prepared by adding the proper volume of this stock solution to 20 cc. of 0.5 *N* sodium hydroxide, and shaking after the mixture had been acidified with 0.6 cc. of glacial acetic acid. After the further addition of 4 cc. of the Griess reagent, dilution to 27 cc., and thorough mixing, the solutions were allowed to stand 20 minutes before their transmissions were measured on the spectrophotometer in a cylindrical quartz cell (inside length, 5.15 cm.; inside diameter, 2.40 cm.).

TABLE I. CONCORDANCE OF CURVES

After 20 Minutes' Standing. $I_B = 76.2\%$						
	0.50	1.00	2.00	4.00	6.00	10.00
(calcd.)	0.049	0.0785	0.1488	0.3115	0.4620	0.7816
	0.098	0.0785	0.0744	0.0779	0.0770	0.0782
	0.63	1.02	1.93	4.03	5.99	10.1
Av. $k = 0.0772$						
After 50 Minutes' Standing. $I_B = 75.7\%$						
	0.50	1.00	2.00	4.00	6.00	10.00
(calcd.)	0.050	0.0777	0.1483	0.3074	0.4591	0.7753
	0.101	0.0777	0.0742	0.0769	0.0765	0.0775
	0.65	1.01	1.94	4.02	5.99	10.1
Av. $k = 0.0766$						

The standard solutions were prepared in this way mainly because aqueous sodium hydroxide was used as absorbent in the nitric oxide determinations; thus the troublesome purification of the reagents could be circumvented. Also, the sodium acetate, by decreasing the acidity, may speed up the reactions involved in the formation of the azo dye. The transmission curves for the standard nitrite solutions are shown in figure 1.

The maximum absorption of visible light by the azo dye evidently occurs at 5200 Å., and this wave length was accordingly chosen for quantitative colorimetric work. Beer's law in the form

$$\Delta = \log I_B/I = k(m) \quad (1)$$

where  $I_B$  is the intensity of transmitted light at 5200 Å. for the reagent blank,  $I$  is the corresponding intensity for the sample, and  $m$  is the micrograms of added potassium nitrite, will be used to show the concordance of the curves at the absorption maximum.

The average  $k$ , which is used in computing  $m$  (calculated), is the arithmetical mean of all values except that for 0.5 microgram. The data show: (1) that above  $m = 0.5$ ,  $m$  and  $m$  (calculated) are in excellent agreement: Beer's law is obeyed within the experimental error (usually less than 2 per cent); (2) that, after the first 20 minutes, standing up to 30 minutes more has little or no effect on the results. This concordance, which might be increased even further, establishes this as one of the more accurate colorimetric methods; it shows that Bennett (2) was correct in attributing his larger (5 to 10 per cent) errors to the personal factors associated with visual comparisons. It suggests that the conversion of nitrite into azo dye, a relatively complex process, is virtually complete even at these very low concentrations of nitrite. The colorimetric method might be a valuable tool for investigating the mechanism of the reactions involved in the conversion.

The molar extinction coefficient of the azo dye can be calculated from  $k$  if complete conversion of the added nitrite is

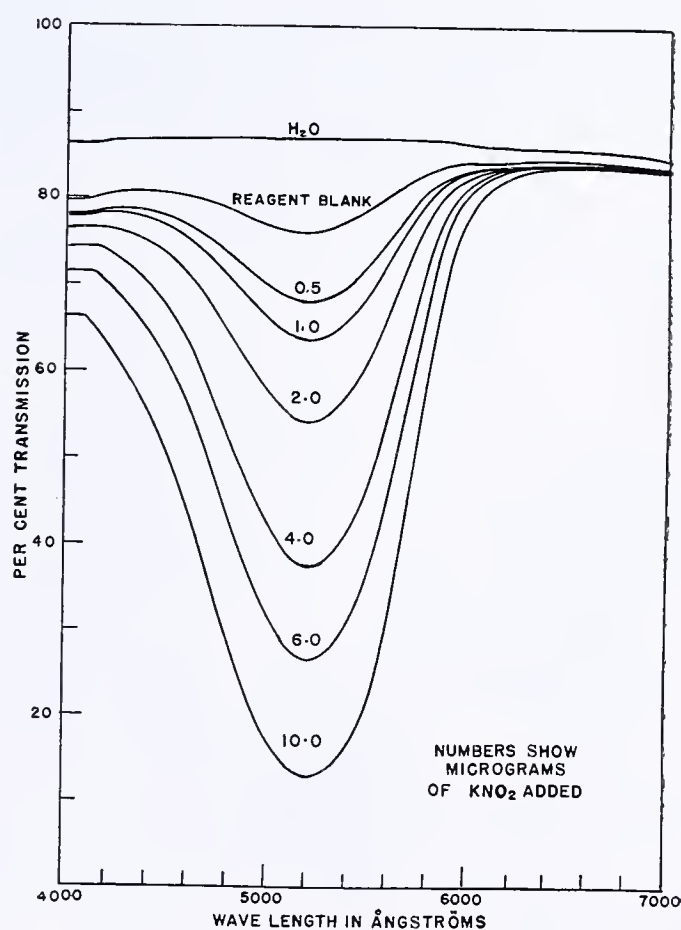
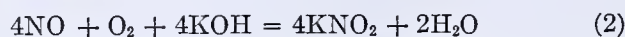


FIGURE 1. TRANSMISSION CURVES OBTAINED WITH THE POTASSIUM NITRITE STANDARD SOLUTIONS



assumed. The result,  $\epsilon = 34,400$  for  $5200 \text{ \AA.}$ , is in close agreement with the maximum coefficients for dithizone ( $30,400$  at  $6200 \text{ \AA.}$ ) and copper dithizonate ( $35,600$  at  $5080 \text{ \AA.}$ ) (13); since the magnitude of  $\epsilon$  is an index of the sensitivity of a colorimetric method, it may be that  $35,000$  or thereabouts is an upper limit that maximum extinction coefficients in colorimetric methods may be expected to approach;  $\epsilon$  of the zirconium-quinalizarin lake, for example, is only  $10,000$  (14).

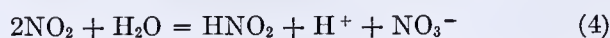
An extensive literature testifies that the stoichiometry of the reaction between nitric oxide and oxygen is a complex and somewhat controversial subject; no complete discussion can be given here. Baudisch and Klinger (1) first proved that the reaction



could be used for the determination of nitric oxide; stoichiometric conversion into nitrite occurs, provided the hydroxide is sufficiently dry (12) and the oxygen is admitted to nitric oxide that is already in contact with the alkali. If these conditions are not carefully observed, the reaction



also occurs. Reaction 3 is known to involve the intermediate formation of nitrogen dioxide, which can react with water (perhaps also with the alkali) to give nitrate and nitrite, for example:



This earlier work would indicate that nitric oxide can never be completely converted to nitrite if it is mixed with an excess of oxygen and permitted to stand in contact with dilute alkali.

It was accordingly necessary to test the stoichiometry of the reaction between nitric oxide and oxygen.

Pure nitric oxide was prepared by reacting potassium nitrite, potassium iodide, and sulfuric acid (9); and was passed through 90 per cent sulfuric acid, then through 50 per cent potassium hydroxide. The resulting gas was diluted with nitrogen and added in known amounts to two 4-liter flasks containing 100 cc. of 0.5 N sodium hydroxide and about 10 cm. of air. Nitrogen sufficient to raise the pressure to about 1 atmosphere was finally added. The flasks were shaken vigorously for a minimum of 10 minutes, whereupon duplicate nitrite determinations were made on aliquot parts of the two alkaline solutions.

TABLE II. NITRITE DETERMINATIONS

Sample	Nitrite Found Micrograms of $\text{KNO}_2$	Nitric Oxide Found	Nitric Oxide Added
		P. p. m.	P. p. m.
1	171	12.7	8.0
1	168	12.5	8.0
2	367	27.2	22.8
2	351	26.0	22.8

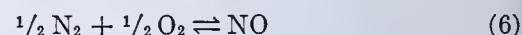
The agreement of duplicate determinations for each sample is good, but about 4 parts per million too much of nitric oxide was found in both cases. This unexplained discrepancy may have been due to nitric oxide introduced as an impurity. At any rate, since the results are high, there is no indication of nitrate formation (Reaction 3). Bennett carried out similar tests—apparently, however, with much less shaking (2, p. 1150, line 9; and p. 1152, Figure 9)—but never obtained complete conversion to nitrite when the concentration of nitric oxide was near 10 parts per million. The authors' results indicate that complete conversion can be obtained in a relatively short time with vigorous shaking, even in contact with aqueous sodium hydroxide and excess oxygen. A likely explanation for this apparent conflict with earlier observations (1, 11, 12) is not difficult to find. There can be little doubt that nitrate formation is usually preceded by the formation of nitrogen dioxide (Reaction 4), since nitrate formation is enhanced by the presence of water or of excess oxygen. The

gaseous reaction by which nitrogen dioxide is formed from nitric oxide and oxygen follows the law (10)

$$-d(\text{O}_2)/dt = k (\text{NO})^2 (\text{O}_2) \quad (5)$$

Equation 5 predicts that nitrogen dioxide formation will be retarded by reducing the nitric oxide pressure; consequently no nitrate may have formed in the authors' experiments because the nitric oxide pressure was too low. But the whole subject deserves further attention—a kinetic investigation, using the colorimetric method, of the oxidation of nitric oxide at very low pressures by oxygen in the presence and absence of aqueous sodium hydroxide should yield interesting and important information.

Samples of furnace atmospheres were successfully analyzed by the method used in the experiments with nitric oxide. When no oxygen detectable in an ordinary gas analysis was present, results below 1 part per million of nitric oxide were consistently obtained, showing that the discrepancy of 4 parts per million encountered above is not inherent in the analytical method. When a gas containing 0.7 per cent oxygen, 9.7 per cent carbon dioxide, no carbon monoxide, and 89.6 per cent nitrogen issued from a furnace in which the maximum temperature was  $1390^\circ \text{C.}$ , about 80 parts per million of nitric oxide were found. This concentration is about one seventh the equilibrium concentration for the reaction



at  $1390^\circ \text{C.}$  and far above the concentration for room temperature (3), indicating that the mixture of gases cooled rapidly enough to slow up the dissociation of nitric oxide (of course, equilibrium at  $1390^\circ \text{C.}$  may never have been established). The colorimetric method might be used to study the rate of the reverse, and perhaps of the forward, reaction in the important Equilibrium 6.

Attempts to collect the nitric oxide by passing the furnace gas mixed with air through liquid air and then through a bubbler containing dilute sodium hydroxide were unsuccessful, probably because there was insufficient time for the conversion of nitric oxide to nitrite.

## Summary

The determination of very small amounts of nitrite with Griess's reagent (sulfanilic acid and  $\alpha$ -naphthylamine in acetic acid solution) has been studied with a recording spectrophotometer and found to be one of the more accurate colorimetric methods.

The same reagent has been used successfully for the determination of nitric oxide in concentrations well below 10 parts per million.

The possible use of the colorimetric method in several other connections has been pointed out.

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# Identification of Lines in Qualitative Spectrographic Analysis

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Charts giving a wave-length scale, an iron arc reference spectrum, and analysis lines for 47 elements are constructed for the region 2500 to 5150 Å. by use of a quartz Littrow spectrograph. Directions are given for using the charts in spectrographic qualitative analysis. Reproductions of the charts may be used as accurate wave-length and analysis scales for any quartz spectrograph.

A COMPLETE spectrographic analysis for fifty or more elements is a tedious procedure, usually done by comparing the analysis spectrum with standard plates or by using enlargements of standard spectra. A method of identification has been used in this laboratory that has materially shortened the labor of an analysis, and is believed to be fully as reliable as other methods. The procedure is to project an enlarged image of the analysis spectrum onto a chart which contains a standard spectrum map, an iron arc reference spectrum, and a wave-length scale. The standard map gives the important analysis lines of all elements sought. Instead of identifying all lines or looking for specific lines of various elements, it is necessary only to note coincidences of projected lines with lines of the map.

The complete set of charts is shown in Figure 1. There are nine charts, each inked on a stiff card measuring 15 × 2.5 cm. (6 × 25 inches). Each card corresponds to a plate region of 3.8 to 4.4 cm. (1.5 to 1.75 inches), five cards being required for examination of a completely filled 10 × 25 cm. (4 × 10 inch) plate. There is some overlapping of the spectral regions covered by successive cards, so that a line may be identified in one section and then be used as a reference point for beginning the examination of the following section.

## Construction of Charts

The wave-length or dispersion scale was first constructed by use of an iron arc spectrum. Selected lines, at convenient intervals, were identified by use of a standard grating spectrum and the wave lengths of these lines were ascertained by reference to Kayser's (2) tables. The spectrum was now projected, at a magnification of 13×, onto the x-axis of a large sheet of carefully prepared paper and the positions of the selected lines were carefully marked. A wave-length curve was next plotted on the same sheet and selected values at 10 or 20 Å. intervals were projected from the curve onto the x-axis. These integral wave-length values were transferred to cardboard sheets and each interval was subdivided into equal portions for the unit values shown in the charts. The positions of the selected iron lines were also transferred to the cardboard and these lines were inked just below the scale, to serve as a guide for projection at exactly the same magnification as that employed in the original construction. Finally, the analysis lines of the more important elements are marked on the charts.

The spectrum of each element was photographed separately, each accompanied by an iron arc reference spectrum placed directly above the sample spectrum by means of a slit diaphragm. The diaphragm has an opening 1 mm. in height for the iron spectrum and 1.5 mm. in height for the spectrum of the sample. The projected iron lines are the same height as the lines of the sample. The spectra were projected onto the cardboard, the iron lines exactly matched to those of the iron map, and the

positions of the most important lines of the sample marked. The selection of analysis lines was made by inspection of the plate and was confirmed by reference to the tables of Gerlach and Riedl (1) and of Ryde and Jenkins (3).

## Table of Analysis Lines

In order to facilitate use of the charts the analysis lines shown have been listed in Tables I and II, which cover, respectively, the two regions for which the spectrograph is usually set. The ultimate test for the identification of an

TABLE I. ANALYSIS LINES IN REGION 2490 TO 3280 Å.

(More important lines for each element in bold-face type. Important lines in other regions designated by parentheses)

Ag	<b>3281a</b>
Al	2568b, 2575b, 3082b, <b>3093a</b>
As	2493b, 2745b, <b>2780a</b> , 2860a, 2899b, ( <b>2350</b> )
Au	<b>2676a</b> , ( <b>2428</b> )
B	<b>2497a</b> , <b>2498a</b>
Be	<b>3130a</b> , ( <b>2349</b> )
Bi	2898b, 2938b, 3024b, <b>3068a</b>
Cd	2881b, 2980b, <b>3261a</b> , ( <b>2288</b> )
Co	3044a, 3062b, 3072b, 3087b, 3121b, ( <b>3454</b> )
Cr	2836b, 2843b, 2850b, 2986-7a, 3015a, 3017a, 3021a, ( <b>4254</b> , <b>4275</b> , <b>4290</b> )
Cu	<b>3248a</b> , <b>3274a</b>
Fe	See iron map
Ga	2660a, 2720a, 2874a, <b>2944a</b> , ( <b>4172</b> )
Ge	2593b, <b>2651a</b> , 2691b, 2710b, 2754a, 3039a, 3269a
Hg	<b>2537a</b>
In	3039b, <b>3256a</b> , ( <b>4511</b> )
Ir	2544b, 2640b, 2665b, 2694b, 2824b, 2850a, 2925a, 3133a, <b>3221a</b>
Mg	2776-83(5 lines)b, <b>2796a</b> , <b>2803a</b> , <b>2852a</b>
Mn	<b>2576a</b> , 2594a, 2606a, <b>2795a</b> , 2798a, 2801a
Mo	<b>3133a</b> , 3158b, 3170a, 3194a, 3208b, ( <b>3798</b> )
Ni	<b>3002a</b> , <b>3051a</b> , 3054b, 3058b, 3102b, ( <b>3415</b> , <b>3525</b> )
Os	2637b, 2838a, <b>2909a</b> , 3018a, 3031b, <b>3059a</b>
P	2534b, <b>2536a</b> , <b>2553a</b> , 2555b
Pb	2577b, 2614a, 2663b, 2823b, <b>2833a</b> , 2873b
Pt	2651b, <b>2659a</b> , 2707a, 2734b, 2830b, 2998a, 3043a, <b>3065a</b>
Sb	2528a(Si), <b>2598a</b> , 2718b, 2770b, 2878a
Si	2507b, 2514b, 2516a, 2519b, 2524b, 2528b, <b>2882a</b>
Sn	2547b, 2707a, <b>2840a</b> , 2863a, 3009b, 3034a, <b>3175a</b> , <b>3262a</b>
Ta	2648a, <b>2653a</b> , <b>2715a</b>
Th	<b>2837a</b> , ( <b>3741</b> , <b>4019</b> )
Ti	2611a, 2641a, 2644a, 2647a, 2942a, 2949a, 2956a, 3079a, 3088a, 3200a, <b>3235-37-39-42a</b>
Tl	<b>2768a</b> , 2918b, 3230b, ( <b>3776</b> )
V	2908b, 2924b, 3051a, 3054a, 3056a, 3061a, 3066a, 3093a, <b>3102a</b> , 3110a, 3118a, 3125a, <b>3183-4-6a</b>
W	2589a, 2658a, 2724a, 2832a, 2896a, <b>2944a</b> , <b>2947a</b> ( <b>4009</b> )
Zn	3076b, <b>3282a</b>

element is based on the important lines, shown in bold-face type. The symbols "a" and "b" denote the stronger and weaker lines, respectively, both in charts and in the tables. No attempt has been made to separate arc and spark lines, but all classifications are based on the apparent intensities in spectra taken with a direct-current carbon arc operated at 10 amperes from a 220-volt source (the drop across the arc is about 45 volts). Because of the use of a carbon arc, certain of the strong lines listed by Gerlach and Riedl have not been included when these lines fall in a region in which the CN bands have high intensity; rather an attempt has been made to choose lines which fall in a region of low background intensity. For example, the identification of chromium is based on the lines at 4254, 4275, and 4290 Å. rather than on the stronger lines at 3579 and 3594 Å., because the latter lines fall in a region of high band intensity.







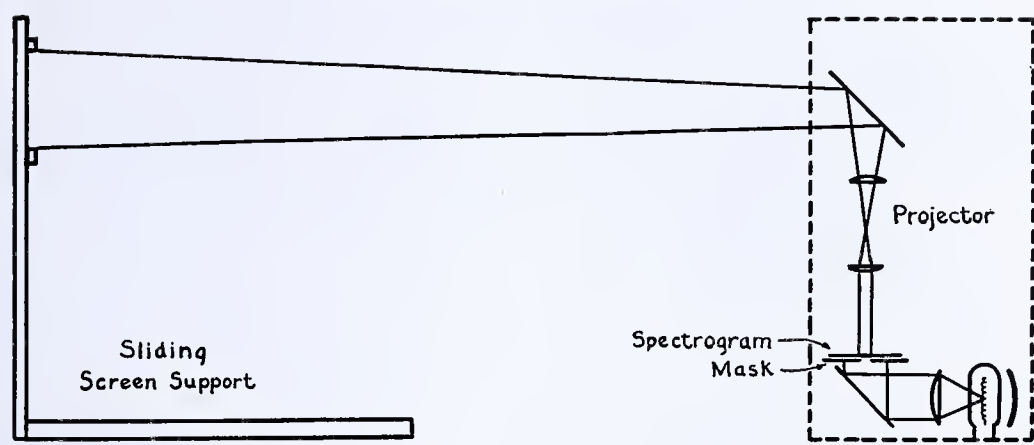


FIGURE 2. ARRANGEMENT FOR PROJECTION OF SPECTRA

TABLE II. ANALYSIS LINES IN REGION 3230 to 5150 Å.  
(Important lines in other regions designated by parentheses)

Ag	3281a, 3383a
Al	3944a, 3962a
Ba	3501b, 4554a, 4934a
Ca	3350b, 3361b, 3631b, 3644b, 3934a, 3968a, 4227a
Cd	3261a, 3404b, 3466-7a, 3611a, 4800a, 5086a, (2288)
Co	3405a, 3412a, 3444b, 3449b, 3453a, 3502a, 3894b, 3995b
Cr	3579a, 3593a, 3605a, 4254a, 4275a, 4290a
Cs	4555a, 4593a
Cu	3248a, 3274a
Ga	4033a, 4172a
In	3256a, 3259b, 4102a, 4511a
K	4044a, 4047a
Li	3233b, 4603a
Mo	3194a, 3209a, 3358b, 3903a
Na	3302-3a (Zn), (5890-6)
Ni	3415a, 3446a, 3458a, 3462a
Pd	3243a, 3405a, 3421a, 3609b, 3634a
Rb	4202a, 4216a(Sr)
Rh	3397b, 3435a, 4375a
Ru	3437a, 3499a, 3635a, 3661a, 3727-8a
Sn	3262a
Sr	4078a, 4216a, 4607a
Th	3188a, 3741a, 4019a, 4276b, 4281b, 4381a, 4392a, 4863a, 4920a
Ti	3200a, 3235-37-39-42a, 3342a, 3370-1-3a, 4301a
Tl	3230b, 3519a, 3529a, 3776a, (5351)
U	4090a, 4242a
V	3184-5a, 4379a, 4385a, 4408a
W	4009a, 4074b, 4295a, (2944)
Zn	3282a, 3303a, 3345a, 4680a, 4722a, 4811a
Zr	3392a, 3438a, 3496a

must be made to coincide with the chart before this is used for analyses.

Use of Charts in Analysis

Each sample spectrum is accompanied by an iron arc reference spectrum, placed directly above that of the sample. The two spectra are projected onto the chart and the magnification is adjusted to bring the iron spectrum into exact coincidence with the iron lines of the chart. It is not necessary to bring an entire section into exact coincidence, but the examination is made in successive small regions by sliding the chart so that it coincides in the desired region. When the iron lines are in coincidence the presence of any element of the chart is shown by coincidence of projected lines with map lines, provided there has been no displacement of the plate holder between the exposures for the iron arc and the sample. (If the sample contains iron, as is often the case, an inspection of the iron doublet near 2600 Å. shows whether or not there has been any displacement of the plate holder during the exposures.)

A single coincidence with the chart does not usually establish an analysis, but in most cases an analysis can be considered positive if all the "a" lines are observed. If the analysis seems doubtful, the tables of Gerlach and Riedl (1) are next consulted and the possibilities of interfering substances are examined. The final test, seldom needed except in the case of very complex spectra, is to prepare a spectrum of a sample of known purity and to identify from the charts the lines of the sample not found in the sample of known purity.

In certain analyses it is desirable to determine the wave length of some lines and to consult Kayser's tables. To determine the wave length of a line the adjacent iron lines are first adjusted to their exact scale positions, as given in Kayser's tables. Then the wave length of the sought line is read directly from the scale. At the magnification usually employed an accuracy of 0.1 Å. is readily attainable in the region below 2700 Å.

Use of Charts for Other Spectrographs

The charts were constructed for use with a Hilger E1 quartz spectrograph, and it was not anticipated that they would be generally useful for spectra taken with other instruments. It has been found, however, that spectra from other quartz Littrow spectrographs will fit the charts closely enough to enable these charts to be used for analysis. In some cases the spectra cannot be made to coincide over the entire length of a section, but it is sufficient to have coincidence over a space of a few inches at each setting. Smaller copies of the charts have even been used successfully for examination of spectra from a medium quartz spectrograph.

At present photostatic copies of the charts<sup>1</sup> are used in this laboratory. These are of slightly reduced size, each section being 52.5 cm. (21 inches) in length, but no detail is lost in this reduction. For use with a medium quartz spectrograph it has been found advantageous to construct a chart with the sections 25 to 30 cm. (10 to 12 inches) in length, using copies of the wave-length scale but redrawing the iron and analysis lines so that they are 1.25 cm. (0.5 inch) in length.

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<sup>1</sup> Additional copies may be obtained from the Photographic Department, University of Chicago, Chicago, Ill., at a price of \$2.00 for the complete set of nine sections.



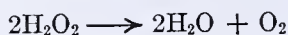
# Determination of Hydrogen Peroxide and Some Related Peroxygen Compounds

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BOOKS recently published in German by Machu (16) and by Kausch (11) include a review of methods for the determination of peroxygen compounds. This paper, which presents a critical discussion of the chief methods for the determination of peroxygen compounds, places special emphasis on the methods which have been used or tested in this laboratory.

The inorganic peroxygen compounds of commerce, hydrogen peroxide, sodium peroxide, sodium perborate, and the peroxides of calcium, barium, strontium, magnesium, and zinc behave similarly from an analytical point of view. These peroxygen compounds may be considered as variations of hydrogen peroxide, since in solution they all display the properties of  $\text{H}_2\text{O}_2$ , probably owing to the presence of the common  $\text{HO}_2^-$  ion (3). Analysis of these products consists in a determination of their active oxygen content—i. e., the oxygen given up when they revert to the oxide. For example,



This may be determined in three basically different ways: by titration, by measuring the volume of oxygen evolved on complete decomposition, and by a colorimetric method. The results may be expressed as per cent of active oxygen, or as per cent of hydrogen peroxide (or other peroxide). The most commonly used term for expressing the active oxygen content of peroxide solutions is volume concentration. This is defined as the number of cubic centimeters of oxygen gas, measured at 0° C. and 760 mm. pressure, liberated from 1 cc. of the solution (measured at 20° C.) when the peroxide is completely decomposed. This may be converted into per cent of hydrogen peroxide by use of the expression

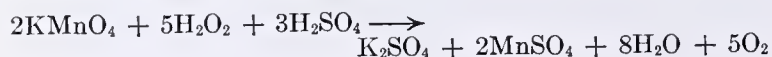
$$\text{Per cent of } \text{H}_2\text{O}_2 \text{ by weight} = \frac{\text{volume concentration} \times 0.30385}{\text{density}}$$

where the volume concentration and density (grams per cc.) are both measured at 20° C., and the factor 0.30385 is based on a molar volume of 22.3927 liters for oxygen gas. The density of solutions of hydrogen peroxide in water has been determined by Maass and Hatcher (15). From their density values the volume concentration may be calculated with an accuracy of 1 per cent from the expression

$$\text{Volume concentration} = 1000 (\text{density} - 1)$$

## Titration Methods

POTASSIUM PERMANGANATE TITRATIONS. The simplest and most commonly used method for determining hydrogen peroxide is by titration with potassium permanganate. This titration is based on the reaction



A critical review of titration methods, decomposition methods, and colorimetric methods for determining active oxygen in the commercial peroxygen compounds is presented in this paper. The principal analytical procedures are outlined and their advantages and limitations are discussed. A new potentiometric method is presented for determining active oxygen in highly colored peroxide solutions containing organic matter.

This method cannot be applied in the presence of organic matter or other substances which reduce permanganate, but in their absence it gives accurate results. In this laboratory the following two procedures have been found satisfactory for titrating samples of 10-volume (3 per cent) hydrogen peroxide or stronger.

A 1-cc. sample of the solution to be tested is measured out with an Ostwald-Van Slyke capillary pipet and to this are added 50 cc. of 20 per cent sulfuric acid. It is then titrated with 0.1786 *N* potassium permanganate until a permanent rose color is obtained. The volume concentration of the solution is equal to the number of cubic centimeters of potassium permanganate used in titration.

As an alternative procedure a 10-cc. sample of the solution under test is diluted to 250 cc. and a 10-cc. aliquot of this is taken for titration. This procedure involves more manipulation than the previous method, but does not require a 100-cc. buret nor an accurately calibrated 1-cc. pipet.

If the concentration of the sample to be tested is less than about 10 volumes, larger samples must be used in both methods.

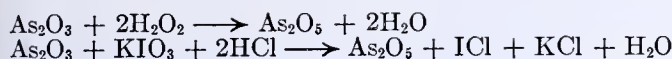
A fading end point in this reaction is indicative of the presence of organic matter or other reducing agents, and if fading persists and high accuracy is desired, the permanganate titration cannot be relied upon. In colored solutions where the end point is difficult to observe, the addition of one or two drops of an oxidation-reduction indicator will be found helpful. The ferrous sulfate complex of *o*-phenanthroline, which has been recommended by Willard and Young (22) for use in ceric sulfate titrations, has been found to be an aid in the potassium permanganate titration of colored solutions.

POTASSIUM IODIDE-THIOSULFATE TITRATIONS. The method which comes next to the permanganate titration in utility is the potassium iodide-sodium thiosulfate titration, which depends upon release of iodine from potassium iodide by the hydrogen peroxide and subsequent titration of the liberated iodine with standard sodium thiosulfate. This method was described by Kingzett (12) and on the suggestions of Kolthoff (14) and of Rothmund and Burgstaller (19) has been improved by the use of ammonium molybdate as a catalyst for accelerating the liberation of the iodine. As used in this laboratory the procedure is to acidify the sample with 20 per cent sulfuric acid, then add 1 cc. of 10 per cent ammonium molybdate solution and an excess of potassium iodide, and titrate with 0.1 *N* sodium thiosulfate, using starch as an indicator. For the analysis of materials which are not water- or acid-soluble, a modification of this method described by Greenbank and Holm (6) is used, using chloroform as solvent and acetic acid instead of sulfuric acid.

The potassium iodide method is of general utility, particularly when the permanganate method fails, but it cannot be used in the presence of other oxidizing agents or unsaturated compounds which react with the free iodine.

SODIUM ARSENITE TITRATIONS. A method has been described by Jamieson (9) which employs the oxidation of arsenite solutions according to the equations:





According to the recommended procedure, 10 cc. of 10 per cent sodium hydroxide are added to a quantity of 0.2 *N* arsenic trioxide sufficient to provide an excess beyond that required to react with the hydrogen peroxide in the sample. The sample is then added and the mixture allowed to stand for 2 minutes, after which 40 cc. of concentrated hydrochloric acid are added, followed by 6 to 7 cc. of chloroform. The residual arsenic trioxide is titrated with 0.2 *N* potassium iodate solution. Rupp and Siebler (20) have described a somewhat similar method in which the solution is made alkaline, diluted with water, and titrated to a colorless end point with standard potassium bromate, using methyl orange as an indicator.

Arsenite titrations are claimed to be affected less by organic matter than the permanganate method, but they obviously cannot be used in the presence of other compounds which are oxidizing towards arsenite solutions.

**TITANIUM TRICHLORIDE TITRATIONS.** One of the oldest methods for the determination of hydrogen peroxide in the presence of organic matter is that of Knecht and Hibbert (13) who made use of the oxidation of titanium trichloride solutions by hydrogen peroxide. When an acid solution of hydrogen peroxide is titrated with titanium trichloride, the color is at first yellow which changes to a deep orange and finally to a colorless end point. The over-all equation is



The titanium trichloride is standardized against a ferric chloride solution using potassium thiocyanate as an indicator. This method has the disadvantages that the end point is difficult to determine and the titanium trichloride solution requires frequent standardization.

**CERIC SULFATE TITRATIONS.** A more recently developed method for hydrogen peroxide in the presence of organic matter is titration with ceric sulfate solutions:



This was first carried out potentiometrically in sulfuric acid solution by Atanasiu and Stefanescu (2). A further potentiometric investigation by Furman and Wallace (5) showed that the titration is also satisfactory in the presence of hydrochloric, nitric, and acetic acids. The use of the previously mentioned *o*-phenanthroline indicator in the ceric sulfate titration makes the end point sufficiently pronounced for visual detection. This method is well adapted for use with solutions containing organic matter or hydrochloric acid, either of which may prevent the use of potassium permanganate.

**POTENTIOMETRIC TITRATIONS.** Potentiometric titrations for hydrogen peroxide have been used chiefly for determining it in mixtures with permonosulfuric acid and persulfuric acid.

Rius (18) described the analysis of such a mixture using a potentiometric titration with sodium sulfite as the reducing agent. The total oxidizing power—i. e., the sum of hydrogen peroxide, Caro's acid ( $\text{H}_2\text{SO}_5$ ), and persulfuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ )—was determined by adding an excess of ferrous sulfate and titrating the excess with potassium permanganate. The sum of hydrogen peroxide and permonosulfuric acid was then determined potentiometrically with sodium sulfite, using a normal calomel cell and a platinum electrode. The hydrogen peroxide was determined by a modified permanganate method which consists in instantaneous mixing of approximately the total titer of potassium permanganate with the sample and proceeding then by trial and error to determine the correct titer.

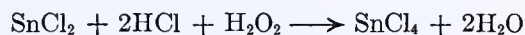
The analysis of mixtures of hydrogen peroxide and permonosulfuric acid was carried out potentiometrically by Müller and Holder (17), who titrated the permonosulfuric acid with potassium iodide, adding benzene to prevent precipitation of iodine on the platinum electrode, then adding sodium acetate as a buffer, and titrating the hydrogen peroxide with bromine in potassium bromide solution.

A convenient and reliable method for determining hydrogen peroxide, permonosulfuric acid, and persulfuric acid when all three are present, is the subject of a current investigation in this laboratory.

With the object of developing an accurate and convenient analytical method for determining hydrogen peroxide in highly colored solutions containing organic matter, the authors have investigated a number of potentiometric titrations, using a mercurous sulfate half-cell and a gold electrode. The following reagents were included in this study: potassium permanganate, ferrous ammonium sulfate, sodium thiosulfate, sodium arsenite, stannous chloride, titanium trichloride, sodium sulfite, and sodium nitrite. The most suitable titrating agent found was sodium nitrite.

Acid solutions of hydrogen peroxide can be accurately titrated potentiometrically with a standard potassium permanganate solution. The potentiometric end point checks exactly with the colorimetric end point and shows a change in e. m. f. of over 400 millivolts for one drop of the reagent. However, potassium permanganate cannot be used for potentiometrically determining active oxygen in solutions containing organic matter, since in that case no sudden change in e. m. f. occurs to indicate the end point.

Ferrous ammonium sulfate, sodium thiosulfate, and arsenious oxide solutions are likewise not satisfactory for the potentiometric titration of hydrogen peroxide, since no sudden change of e. m. f. occurs with either cold or hot solutions even in the absence of organic matter. According to Jellinek and Krebs (10) stannous chloride reacts quantitatively with hydrogen peroxide.



The authors' investigations have confirmed this at temperatures of 75° to 90° C. but the reaction is slow and takes several minutes to come to equilibrium after each addition of the titrating agent. The addition of a catalyst (copper, iron, chromium, and manganese) accelerates the reaction but even under these conditions the titration is still much too slow to be of practical use.

The titration of hydrogen peroxide solutions with titanium trichloride can be followed potentiometrically. The maximum break in the e. m. f. is in the order of 150 to 200 millivolts per drop of 0.1 *N* reagent, but this occurs about 0.3 cc. beyond the colorimetric end point. However, in the presence of organic matter the potentiometric titration is not satisfactory, since there is a rapid change in potential throughout the titration, and there is no evidence of a pronounced break at the equivalent point.

Acid solutions of hydrogen peroxide have been potentiometrically titrated with sodium sulfite (10), the change in e. m. f. at the end point being about 150 millivolts. However, this titration is not satisfactory; the sulfite solution is unstable, the gold electrode loses its sensitivity, and the potential drifts on approaching the end point of the reaction.

Hydrogen peroxide in acid solution can be accurately titrated with sodium nitrite solutions, either in the presence or absence of colored organic matter. The change in e. m. f. at the equivalent point is 150 to 200 millivolts at 90° C. The titration can best be carried out by adding a nearly equivalent amount of the nitrite solution to the acidified hydrogen peroxide, heating to 90° C., and continuing the titration. By this procedure only low concentrations of hydrogen peroxide are heated and hydrogen peroxide decomposition losses are negligible. In titrating the active oxygen in the presence of organic matter it is necessary to add a small concentration of nitric acid, since in its absence determinations of low hydrogen peroxide concentrations are inaccurate.

The following procedure has been found satisfactory for this titration:



Pipet 50 cc. of the hydrogen peroxide solution which has been diluted to about one volume concentration into a 250-cc. beaker and add 50 cc. of distilled water. Acidify the solution with 50 cc. of 20 per cent sulfuric acid and add 5 cc. of *N* nitric acid. Connect the solution to the mercurous sulfate cell by means of a saturated potassium sulfate bridge and titrate potentiometrically with 0.1786 *N* sodium nitrite as follows: (a) Heat the mixture to 90° C. and titrate to the nearest cubic centimeter with the standard sodium nitrite solution; (b) prepare another sample, add nearly an equivalent amount of sodium nitrite as determined in (a), heat the mixture to 90° C., and continue the titration to the nearest 0.1 cc. The change in e. m. f. at the equivalent point is 150 to 200 millivolts. The standard nitrite solution is stable and this method is satisfactory for the determination of hydrogen peroxide in highly colored solutions.

### Decomposition Methods

The fact that hydrogen peroxide decomposes to yield oxygen gas can be made the basis of its analytical determination by measuring the volume of gas which is given off upon complete decomposition. This decomposition may be brought about by a reaction with compounds such as potassium permanganate or sodium hypochlorite (4), or by catalytic decomposition with platinum, manganese, or copper; platinum is the preferred catalyst. These methods are valuable for use with highly colored solutions or in the presence of other oxidizing agents which interfere with titrations but which do not liberate a gas under the conditions of the peroxide decomposition.

### Colorimetric Methods

**POTASSIUM PERMANGANATE.** For the determination of small amounts of peroxide, colorimetric methods can be used. Allen (1) has described a method for the determination of small amounts of hydrogen peroxide by a colorimetric permanganate method. An acid solution of potassium permanganate containing a small amount of magnesium sulfate is treated with the unknown solution and the color is then compared with that of similar solutions containing known amounts of hydrogen peroxide. It is claimed that this method will detect 1 part of hydrogen peroxide in ten million parts of water, but the same limitations must apply to its use as applied in the case of permanganate titrations.

**TITANIUM TRICHLORIDE.** The titanium method finds its chief use colorimetrically and in this laboratory has given good results on solutions containing less than 5 p. p. m. of hydrogen peroxide. It is carried out by adding 3 cc. of a titanium sulfate solution to 100 cc. of the unknown and then matching it against solutions containing known amounts of hydrogen peroxide. The titanium sulfate solution is prepared by treating 1 gram of titanium dioxide with 100 cc. of concentrated sulfuric acid for 15 to 20 hours at about 150° C. and filtering off any undissolved material before using.

**FERRIC THIOCYANATE.** Another valuable method depends upon the formation of the deep red ferric thiocyanate by reaction of hydrogen peroxide in a solution containing ferrous iron and potassium thiocyanate. As described by Horst (?) the method consists of completely reducing a 10 per cent ferric sulfate solution with hydrogen sulfide, flushing out the hydrogen sulfide with carbon dioxide, then adding the unknown and the thiocyanate, and comparing with a standard. The procedure in this laboratory is as follows: Ten grams of the unknown are dissolved in 175 cc. of 20 per cent sulfuric acid and diluted to exactly 200 cc. with water. Half of this serves as a blank and to the other half is added 0.5 cc. of an indicator solution prepared by dissolving 78.4 grams of ferrous ammonium sulfate hexahydrate and 58.3 grams of potassium thiocyanate in 20 per cent sulfuric acid and diluting to 1 liter. This is compared with a solution prepared from a basic standard made up by dissolving 1.7140 grams of potassium thiocyanate and 3.0 grams of ferric ammonium sulfate in 100 cc. of 20 per cent sulfuric acid and then diluting to exactly 1 liter with water. With proper blank corrections it is possible by this method to determine hydrogen peroxide in concentrations up to 0.02 per cent with a high degree of accuracy.

**MISCELLANEOUS COLORIMETRIC METHODS.** The yellow color of permolybdic acid is the basis of a method described by Isaacs (8). The indicated procedure is to add 1 cc. of the unknown to 10 cc. of 5 per cent citric acid in 30 cc. of water; 1 cc. of a 10 per cent solution of ammonium molybdate is then added and the color is compared with solutions containing known amounts of

hydrogen peroxide or with previously standardized solutions of potassium chromate.

Mention should also be made of the recent suggestions of Schales (21) who has discussed the use of Stamm's reagent, fluorescein, and luminol. Many other color reactions have been suggested for use in the analysis of hydrogen peroxide; references to these methods may be found in Kausch's (11) text.

### Related Peroxygen Compounds

**SODIUM PEROXIDE.** Sodium peroxide,  $\text{Na}_2\text{O}_2$ , forms alkaline solutions which behave like alkaline solutions of hydrogen peroxide and may, therefore, be analyzed by the same methods. Solid sodium peroxide is best dissolved for analysis by adding it slowly and with vigorous stirring to an excess of dilute sulfuric acid.

**SODIUM PERBORATE.** Sodium perborate solutions behave like buffered alkaline solutions of hydrogen peroxide and hence may be determined by the methods described for hydrogen peroxide. Solutions for analysis should be prepared from crystalline sodium perborate by dissolving the solid in an excess of dilute sulfuric acid.

**MAGNESIUM AND ZINC PEROXIDES.** The peroxides of zinc and magnesium present no difficulty in analysis, since, although they are not soluble in water, they dissolve readily in sulfuric acid to yield solutions which may be analyzed by the methods given for hydrogen peroxide.

**CALCIUM AND BARIUM PEROXIDES.** The peroxides of barium and calcium are not soluble in water and cannot be dissolved in sulfuric acid. They can, however, be dissolved in dilute hydrochloric acid and if a small sample is used the active oxygen content may be determined by titration with potassium permanganate after the addition of sulfuric acid.

### Summary

The analysis of solutions of peroxygen compounds by titration, decomposition, and colorimetric methods has been discussed.

The permanganate titration is recommended for determining active oxygen in solutions containing neither organic matter nor other reducing substances.

The ceric sulfate titration should be used for solutions containing organic matter or other reducing substances, although some analysts will prefer the iodine-thiosulfate titration which is satisfactory if the organic matter does not contain unsaturated compounds.

A colorimetric method should be used for determining traces of peroxides. The titanium trichloride method is recommended.

A decomposition method may be used for determining active oxygen in highly colored solutions where color changes cannot be detected accurately. A simpler method for use under these conditions, based on potentiometric titration with sodium nitrite, has been developed.

The methods recommended for hydrogen peroxide can also be used for determining the active oxygen in solutions of sodium peroxide, sodium perborate, barium peroxide, calcium peroxide, magnesium peroxide, and zinc peroxide.

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# Standardization of Sodium Thiosulfate by Copper, Using Perchloric Acid

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IN THE available methods for standardizing thiosulfate iodometrically against copper, the copper is dissolved by the oxidizing action of concentrated nitric acid, and various means are used subsequently to eliminate oxides of nitrogen that would interfere in the titration. Among the expedients used, all of them somewhat cumbersome, are the following: addition of sodium hypochlorite and phenol (3); addition of sulfuric acid, evaporation, then addition of hydrochloric acid and further evaporation (1); addition of bromine water and boiling until the excess is removed (8); and the use of urea and boiling (2). Such treatment is followed by the addition of ammonia in slight excess, boiling off the excess, then addition of acetic acid to adjust the acidity.

The method described here consists simply of dissolving copper in concentrated boiling perchloric acid, adding an equal volume of water, boiling for 2 minutes, and diluting to volume. Aliquots are titrated with thiosulfate after addition of potassium iodide using starch and a soluble thiocyanate as described by Foote (1).

Perchloric acid is a good reagent for dissolving copper since solution is fairly rapid on boiling; all the by-products are instantly and completely removed by volatilization (6), while the dilute cold perchloric acid itself does not interfere in the titration (5). No chloride could be detected in solution.

## Reagents

Copper, 99.96 per cent pure (4).  
 Perchloric acid, concentrated (68 to 70 per cent), technical.  
 Potassium iodide, iodate-free, 1 *N* solution.  
 Sodium thiosulfate solution standardized against potassium iodate, the purity of which had been checked against iodine.  
 Starch solution prepared according to Sutton (7).  
 Potassium thiocyanate, reagent grade.

## Procedure

The following procedure applies to the standardization of an approximately 0.025 *N* thiosulfate solution.

To a 0.60- to 0.65-gram sample of copper in a 100-cc. volumetric flask add 6 to 8 cc. of concentrated perchloric acid (about 11 *M*); heat to boiling (hood!). Boil gently until solution is complete, continue boiling for a few minutes, then cool slightly. Add an equal volume of water and boil for 2 minutes to drive off any chlorine that may be still present. After cooling dilute to volume. To 10-cc. portions add 5 cc. of 1 *N* potassium iodide. Let stand for 2 minutes and titrate with sodium thiosulfate until the yellow color is nearly discharged. Add 5 cc. of starch solution

and titrate to near the end point. Add 1.5 to 2.0 grams of potassium thiocyanate (1) and titrate to the disappearance of the blue color. The end point should be checked by the addition of 0.025 *N* iodine, since at the end point the titration mixture is not white but flesh-colored.

TABLE I. STANDARDIZATION OF THIOSULFATE

Normality	Average Error	Number of Titrations
	Against KIO <sub>3</sub>	
0.02484	±0.00002	3
0.02488	±0.00001	3
	Against Cu(ClO <sub>4</sub> ) <sub>2</sub>	
0.02483	±0.00003	6
0.02484	±0.00001	3
0.02486	±0.00002	9
0.02490	±0.00001	3

If 10 to 12 cc. of 5.5 *M* perchloric acid are used, solution will be much slower. Eight cubic centimeters of acid of this concentration will not completely dissolve the copper. Variation of the acid concentration in the copper solution from 0.3 *N* to 0.7 *N* has no apparent effect on the titration value. Greater acidity than this should be avoided, since the amount of thiosulfate consumed tends to become slightly too high (about 0.30 per cent). Titrating under artificial light, the end point tended to appear too early (about 0.25 per cent). No blank correction was necessary.

The mean value against copper as well as against iodate is 0.02486 ± 0.00002.

## Acknowledgment

The copper used in this work was kindly supplied by W. M. McNabb, University of Pennsylvania. The writer wishes to thank G. Toennies of this institute for his suggestions and criticisms.

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# Quantitative Determination of Selenium in Tissues and Feces

## A Photometric Method

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THE recent interest in the toxicology of selenium compounds has resulted in the development of new and exact methods for determining traces of this element in soils and biological material.

Robinson (5), in a search for a quantitative method for determining selenium in plants and soils, acted upon the assumption that selenium might be expected to behave in a general way like sulfur. Accordingly, he developed a method by which selenium could be separated from all elements except arsenic and germanium. This procedure was improved upon shortly thereafter by Robinson, Dudley, Williams, and Byers (6), who made it applicable for amounts of selenium as small as 0.01 mg. Dudley and Byers (1) made it even more suitable for biological materials. The principle involved initial hydrolysis and oxidation of the material, conversion of selenium to the bromide, distillation of the bromide, and reduction to the free element. The selenium precipitate was then filtered off, dried, and weighed, or, in the case of minute amounts reprecipitated in the presence of gum arabic solution, so that the red color of the colloidal selenium could be estimated colorimetrically.

Horn (3) modified an earlier procedure proposed by Schmidt (7) for detecting small amounts of selenious acid in sulfuric acid. Plant materials were digested as in the regular Kjeldahl method with added mercuric oxide, which served to prevent loss of selenium through vaporization. When a few drops of saturated aqueous codeine sulfate were added to aliquot portions of the clear digests, blue colors developed in those tubes containing selenium. By comparing these colors with those of similar standards, a roughly quantitative estimation of the amount of selenium could be made. Vanadium alone interfered in the test. This method was later used by Franke and Painter (2) in the rough determination of the selenium content of toxic grains, but it has not heretofore been applied to the more exact determination of small amounts of selenium in animal tissues and products.

In the course of experiments concerned with chronic selenium intoxication in rats, it was necessary to determine the selenium content of the feces and certain tissues. None of the existing methods proved to be very satisfactory for determining the minute amounts of selenium present in rat tissues; the results were inconsistent and the procedure of Robinson, Dudley, Williams, and Byers (6) as modified by Dudley and Byers (1) involved many steps which required considerable time to complete and increased the chances for loss of selenium. Accordingly, the colorimetric method of Horn (3) was adopted and modified. It is believed that the photometric application of this color reaction is capable of extensive application to the analyses of biological products for selenium.

### Experimental

The samples of dried feces were prepared for analysis by first grinding them in a mortar to ensure uniform mixing. One-gram samples were then weighed out for analysis. In the analysis of tissues, particularly of liver, it was found necessary to effect a preliminary removal of most of the fat, since fat is digested in the Kjeldahl procedure only with great difficulty. Fatty degeneration

of the liver is commonly associated with selenium poisoning in rats. Attempts to analyze livers that had not been defatted resulted in very black and lumpy digests, even after 10 to 15 hours of digestion, despite the fact that during the period of digestion, at intervals of 60 to 90 minutes, small amounts of hydrogen peroxide were added to facilitate oxidation. A preliminary extraction with chloroform was, accordingly, carried out. Since in most cases it was not possible to analyze the tissues immediately after removal from the animal, they were preserved in 10 per cent formalin solution until analyses could be undertaken. The formalin served also to harden the tissues so that they could easily be ground for extraction. Analyses of the formalin in which the organs had been preserved showed that no selenium had been removed.

The fat extractions were carried out as follows: The organs were removed from the preserving fluid, pressed between filter papers to remove most of the liquid, and ground in a small porcelain mortar. The ground tissue was then transferred to a 250-cc. Erlenmeyer flask, 100 cc. of chloroform were added, the flask was connected to a water condenser, and the mixture was refluxed on the steam bath for 3 to 4 hours. The chloroform was then removed from the extracted tissue by filtration, and the residual tissue was washed twice with small portions of hot chloroform, and dried in air at room temperature. Weighed amounts of this dry material were analyzed.

The digestion of a dry sample was carried out in a 100-cc. Kjeldahl flask. Yellow mercuric oxide (0.20 gram) was added and any particles adhering to the neck of the flask were washed down into the flask with 5 to 10 cc. of water, which served also to prevent foaming at the beginning of the digestion. Thirty to 40 cc. of concentrated sulfuric acid were added, with two glass beads to prevent bumping. Digestions were continued for 6 to 8 hours, at the end of which time only a light yellow tinge remained in the solution. The occasional addition of 5 to 10 drops of 30 per cent hydrogen peroxide served to accelerate the oxidation. Upon cooling, the solution became colorless and a white precipitate of mercuric sulfate formed. The cooled digest was trans-

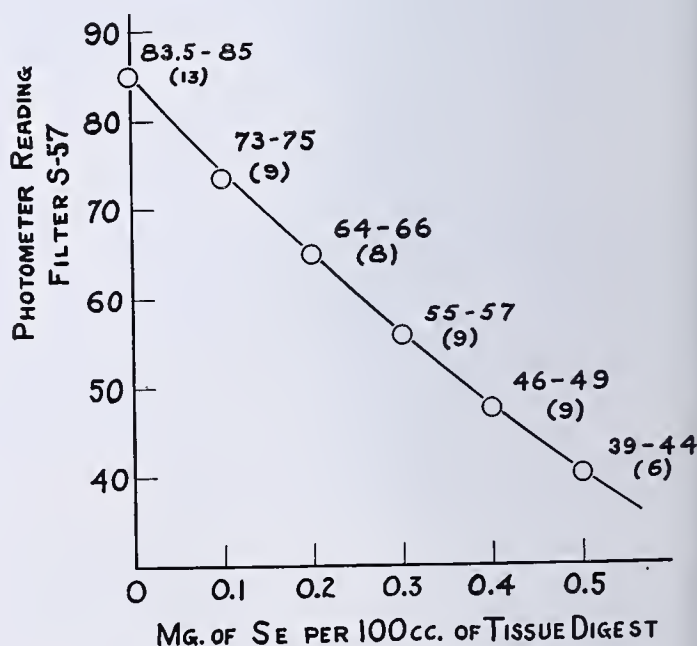


FIGURE 1. STANDARD PHOTOMETRIC CURVE FOR ANALYSIS OF SELENIUM IN TISSUE DIGESTS

Plotted from data in Table II. Figures at each point on curve indicate range of photometric readings; those in parentheses indicate number of determinations for each concentration of selenium.



ferred quantitatively to a 50-cc. volumetric flask, diluted to volume with concentrated sulfuric acid, mixed, and centrifuged for 15 to 20 minutes at approximately 1800 r. p. m. A 10-cc. portion of the clear colorless centrifugate was pipetted into a clean dry test tube and 3 drops of a saturated aqueous solution (3 per cent) of codeine sulfate were added. The tubes were stoppered tightly and placed in a dark cupboard for 7 hours to permit the development of the blue color. The percentage transmission of light of the solution was then determined in a Zeiss-Pulfrich photometer (4), used in the vertical position. A 10-mm. cell containing approximately 5 cc. of solution and the yellow filter S-57 were found most convenient.

TABLE I. INFLUENCE OF TIME OF COLOR DEVELOPMENT ON PHOTOMETER READINGS OF NORMAL FECAL DIGESTS CONTAINING ADDED SODIUM SELENITE

(All readings are for separate determinations)							
Time of Color Development Hours	Concentration of Se, Mg. per 100 Cc. of Fecal Digest						
	0	0.05	0.1	0.2	0.3	0.4	0.5
Photometer Readings <sup>a</sup>							
4	..	..	81	72	61	58	48
5	85	..	81	72.5	60	57	44
	90	..	79.5	66.5	58	51	43
6	..	..	80.5	67	59	47.5	41.5
	91.5	..	80	68	60	57.5	43
	91.5	..	84	69	57	49.5	40
	90	85	76.5	65.5	56.5	50	39
	91	88	81	69	58	56.5	49
7	91.5	..	..	69	..	56	..
	92	85	78	67	57	46	..
8	90	..	79	67.5	58	52	42.5
	92	..	79	69	56	50	42
	90	..	78	66	55	47	..

<sup>a</sup> Expressed as percentage transmission (D per cent).

Standard curves were constructed by measuring the percentage light transmission of the blue solutions obtained with digests to which known amounts of selenium had been added. These standard curves differed slightly for tissues and feces. Digests of known selenium concentration were most simply prepared from a digest of the feces or tissues of normal animals, assumed to be free from selenium, and a similar digest to which sodium selenite had been added to give a selenium content of 0.5 mg. per cent. By appropriate admixture of the two, it was easy to obtain solutions containing from 0.0 to 0.5 mg. per cent of selenium. A typical curve is presented in Figure 1.

Various factors which might influence color development were studied. Horn (3) reported that when the digests took up moisture the blue color faded; accordingly, care was taken to prevent access of air to the acid solutions after the digests cooled. Light was also found to affect the color development. When the tubes were exposed to daylight for a day or more, the blue color turned to purple, while in other tubes kept in the dark for a similar period the change to purple was not noted.

The effect of time on the development of the blue color is shown in Table I. After 4 hours the colors were incompletely developed, while after 6 to 8 hours the photometric readings were consistent. An interval of 7 hours between addition of the codeine sulfate and the photometric estimation was arbitrarily selected.

Since in the analyses of tissues of rats it was not always possible to obtain as much as 1 gram of the dry powdered organs, a study was made to determine the effect of different amounts of tissue in the sulfuric acid digests on color development. As is shown in Table II, reproducible readings were obtained when the amount of dry tissue used for analysis varied from 0.6 to 2.0 grams. The fact that the recovery of added selenium, when digests of 1.5 to 2.0 grams of tissue were used, was no greater than the recovery when 0.6 gram was used in the preparation of the digest is indicative of the absence of any significant amounts of selenium in normal rat tissues.

From the typical data given in Tables I and II, smooth standard curves (Figure 1) were easily constructed. When known amounts of selenium were added to normal rat feces and the analytical procedure was carried out using color-development periods of 6 to 8 hours, the selenium determined was in 75 per cent of the cases within 10 per cent and in 88 per cent of the cases within 15 per cent of the theoretical amount. All the remaining discrepant values were obtained with digests in which the color had been allowed to develop only 6 hours. The values for the tissue digests in Table II, in which a standard time interval of 7 hours was employed, were even more consistent, 98 per cent of the determinations checking to within 10 per cent of the amount of selenium added. In most cases the photometer readings ranged well within the limits of accuracy of the instrument. The results of the application of this method will be presented elsewhere.

TABLE II. EFFECT OF VARYING THE AMOUNT OF TISSUE IN DIGESTS CONTAINING KNOWN AMOUNTS OF SELENIUM

(Seven hours allowed for development of colors)					
Dry Fat-Extracted Tissue Grams	Se Added Mg./100 cc.	Range of Photometer Readings <sup>a</sup>	No. of Determinations	Se Found Mg./100 cc.	Maximum Error %
0.6	0.0	83.5-85	3	0.0-0.01	..
	0.10	73.0-73.5	2	0.1-0.105	5
	0.20	65	2	0.195	3
	0.30	56	2	0.30	0
	0.40	47	2	0.41	3
0.8	0.50	40	1	0.505	1
	0.0	84.5-85	2	0.0-0.005	..
	0.10	73	1	0.11	10
	0.20	64	1	0.205	3
	0.30	56	1	0.30	0
1.0	0.40	47	1	0.41	3
	0.0	85	3	0.0	..
	0.10	73-75	2	0.09-0.11	10
	0.20	65-66	2	0.185-0.195	8
	0.30	56-56.5	2	0.295-0.30	2
1.5	0.40	46-48	2	0.40-0.425	6
	0.50	44	1	0.45	10
	0.0	85	4	0.0	..
	0.10	73.5-74	3	0.095-0.10	3
	0.20	65-66	3	0.185-0.195	10
2.0	0.30	55-57	3	0.29-0.310	3
	0.40	48-49	3	0.39-0.40	3
	0.50	40-42	3	0.48-0.505	4
	0.0	84	1	0.01	..
	0.10	73	1	0.105	5
	0.20	61	1	0.24	20
	0.30	56	1	0.30	0
	0.40	48	1	0.40	0
	0.50	39	1	0.515	3

<sup>a</sup> Expressed as percentage transmission (D per cent).

Williams and Lakin (8) have emphasized the possibility of losses of selenium by volatilization during the period of digestion with acid. This must be considered particularly when large amounts of a sample, rich in materials difficult of digestion, are used in the analyses. The authors have employed the procedure described for the analyses of animal tissues or excreta only. Under these conditions, the method has given consistent and reproducible results which are believed to be reliable.

## Summary

Horn's modification of the codeine sulfate reaction for the detection of selenium has been applied to the quantitative determination of minute amounts of selenium in animal tissues and feces. The dry sample is digested with sulfuric acid and mercuric oxide, cooled, made to volume, and centrifuged. To a portion of the clear digest is added codeine sulfate solution and an interval of 7 hours in the absence of light is allowed for development of the blue color, after which time the transmission of light is determined in the Zeiss-Pulfrich photometer with the use of the yellow filter S-57 (4). The amount of selenium present is easily calculated from standard curves obtained in a similar manner, using digests of normal tissues or feces containing added sodium selenite.



The advantages of the method are the speed with which a given analysis can be carried out, the large number of determinations which can be done within a short time, and the simplicity of the procedure as compared to other existing methods. The use of the photometer makes it possible to obtain accurate readings on solutions in which the depth of color is too slight to be estimated in a colorimeter.

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# Identification of Aldehydes and Ketones

## By Estimation of Hydrazine Nitrogen According to the Jamieson Method

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ALDEHYDES and ketones are frequently identified by the derivatives which they form with hydrazine or one of its substitution products. Semicarbazones can be prepared and purified readily in most instances, and, accordingly, have found extensive application in systematic organic analysis. Analysts rely on the melting point and occasionally the crystal habit of the semicarbazone for the identification of the aldehyde or ketone.

In spite of the importance and great utility of these derivatives, certain limitations are inherent in the methods employed. Difficulties may be encountered in characterizing carbonyl components in complex mixtures from natural sources, or indeed even in mixtures of synthetic solvents. Physical constants of the components and melting points of their derivatives are sometimes changed markedly by the presence of small amounts of impurities. In the investigation of new substances, moreover, the physical properties of derivatives give no aid in the initial characterization of the compounds.

The determination of the hydrazine nitrogen content of a semicarbazone (or other hydrazone) will enable an analyst to compute the equivalent weight of the parent carbonyl compound. If the compound has been characterized previously, he may check its identity as determined by the classical method, or if the compound is new, the equivalent weight may be compared with the molecular weight as measured by one of the familiar physical methods. It has been found in these laboratories that hydrazine nitrogen can be determined in a number of derivatives of hydrazine by the method devised by Jamieson (16), and the experiments described in this paper were undertaken in order to investigate the applicability of the Jamieson method for the determination of hydrazine nitrogen in a series of semicarbazones of certain common aldehydes and ketones. The following semicarbazones were prepared and analyzed by this technique: acetophenone, cyclohexanone, diethyl ketone, acetone, benzophenone, benzaldehyde, cinnamic aldehyde, and furfural. The method is applicable for all semicarbazones studied except furfural semicarbazone. A few isolated experiments on other applications of the Jamieson method are also described.

### Historical

The name hydrazine was applied by Emil Fischer to the hypothetical substance  $N_2H_4$ , which he considered to be the parent substance of phenylhydrazine, isolated in 1875 (11, 14). Curtius isolated the first hydrazine salts in 1887

(5, 6). Piloty, Fischer, Baeyer, and other workers found that hydrazine, and more especially phenylhydrazine (9) *p*-bromophenylhydrazine (10), and semicarbazide (2, 3), were of value in preparing derivatives of carbonyl compounds. Curtius and Jay (7, 8) and others (1) similarly investigated the hydrazides and diacyl hydrazines of organic acids.

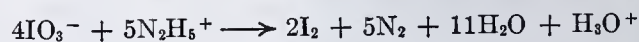
The reducing powers of hydrazine were also the subject of much study. Pechmann found that certain hydrazine compounds could be oxidized to tetrazines (17), and soon many workers were investigating the reduction of potassium iodate by hydrazine (18, 19, 20, 23). In 1912 Jamieson proposed the particular quantitative modification of these methods that now bears his name (15, 16).

In 1931 Botti analyzed cobalt complexes of hydrazine by this method (4). In 1936 and 1937 Fuller employed it for the detection and estimation of aminoguanidine and benzyl aminoguanidine (12, 13). Lastly, Schaeffer and Weinberger have used the Jamieson method to determine the equivalent weights of the hydrazides of kerrolic, aleuritic, and isoaleuritic acids (21, 22, 24, 25). Their results in all cases agree closely with the molecular weights determined by the Rasch method.

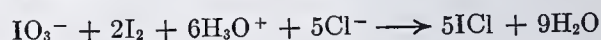
### Experimental

**ANALYTICAL METHOD.** Samples of the hydrazine compound are transferred to 150-ml. glass-stoppered bottles, 20 ml. of water and 30 ml. of concentrated hydrochloric acid are added, and the sample is dissolved and hydrolyzed simultaneously. Chloroform or carbon tetrachloride is added and the mixture is titrated with an 0.1 *N* solution of potassium iodate. Between addition of the reagent the stoppered bottle is shaken vigorously.

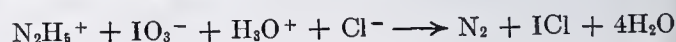
On the first addition of reagent free iodine appears in the chloroform layer and on further addition reaches a maximum. This stage of the reaction may be formulated as follows:



On further addition of reagent the iodine color is discharged and the final disappearance of the iodine color in the chloroform layer is taken as the end point. This end point may be located to within one drop of 0.1 *N* reagent. The second stage of the reaction may be represented as follows:



Hence the stoichiometrical equation for the complete reaction is written as follows:





The standard solution is prepared by dissolving 3.567 grams of potassium iodate in water and diluting to 1 liter. This 0.1 *N* solution should be standardized against recrystallized hydrazinium sulfate and 1 ml. of this solution is equivalent to 0.00217 gram of hydrazinium sulfate or 0.000534 gram of hydrazine.

**PREPARATION OF MATERIALS.** The semicarbazones are prepared by adding a warm aqueous solution containing equal amounts of semicarbazide hydrochloride and sodium acetate to the aldehyde or ketone, and agitating the mixture vigorously in a stoppered bottle or flask. The crystals of the semicarbazone are separated by filtration on a Büchner funnel, washed, and finally recrystallized from alcohol.

In the case of acetone, the following procedure is employed: twenty-five grams of semicarbazide hydrochloride in saturated aqueous solution are added to 21.8 grams of sodium acetate in an alcoholic solution. The solution is cooled to 0°, 12.9 grams of acetone are added, and the mixture is warmed. After standing for approximately 16 hours, the crystals are separated. If more acetone is added to the mother solution more semicarbazone may be obtained.

Benzophenone semicarbazone is prepared in the following manner: A weighed portion of benzophenone is dissolved in alcohol and water is added until cloudiness appears, whereupon alcohol is added to clear the solution. An approximately equivalent quantity of semicarbazide hydrochloride is added together with the same weight of sodium acetate. The solution is heated under a reflux for several hours, cooled, and the benzophenone semicarbazone is separated on a Büchner funnel.

TABLE I. ANALYSES

Compound	Substance Taken Gram	Weight Found Gram	Error %
ure hydrazine sulfate	0.0414	0.0416	+0.5
	0.0242	0.0245	+1.2
	0.0763	0.0769	+0.8
	0.0725	0.0724	-0.1
micarbazide hydrochloride	0.0628	0.0629	+0.2
	0.0523	0.0522	-0.2
	0.0476	0.0481	+0.8
	0.0593	0.0595	+0.3
etophenone semicarbazone M. p. found, 197-199° C. M. p. reported, 198° C.	0.0532	0.0531	-0.2
	0.0656	0.0661	+0.8
	0.0543	0.0545	+0.4
	0.0641	0.0639	-0.3
ude cyclohexanone semicarbazone	0.0525	0.0527	+0.4
	0.0470	0.0489	+4.0
	0.0408	0.0427	+4.7
	0.0668	0.0713	+9.7
rified cyclohexanone semicarbazone M. p. found, 165-167° C. M. p. reported, 166-167° C.	0.0466	0.0478	+2.6
	0.0214	0.0217	+1.4
	0.0115	0.0111	-3.5
ethyl ketone semicarbazone M. p. found, 138° C. M. p. reported, 139° C.	0.0403	0.0403	0.0
	0.0370	0.0369	-0.3
	0.0540	0.0550	+1.9
	0.0364	0.0362	-0.6
etone semicarbazone M. p. found, 187.5-188.5° C. M. p. reported, 187° C.	0.0581	0.0606	+4.3
	0.0542	0.0543	+0.2
	0.0597	0.0604	+1.2
	0.0340	0.0338	-0.6
enzophenone semicarbazone M. p. found, 154-164° C. M. p. reported, 167° C.	0.0669	0.0678	+1.3
	0.0814	0.0809	-0.6
	0.0442	0.0448	+1.4
	0.0575	0.0561	-2.4
nzaldehyde semicarbazone M. p. found, 212-213° C. M. p. reported, 222° C.	0.0466	0.0457	-1.9
	0.0400	0.0394	-1.5
	0.0824	0.0821	-0.4
	0.0265	0.0262	-1.0
nnamic aldehyde semicarbazone M. p. found, 208° C. M. p. reported, 208° C.	0.0457	0.0447	-2.2
	0.0417	0.0413	-1.0
	0.0607	0.0603	-0.7
	0.0269	0.0276	+2.6
	0.0605	0.0593	-2.0
	0.0201	0.0197	-2.0
	0.0303	0.0298	-1.7

**ANALYSES.** The standard solution of potassium iodate as employed first for the determination of hydrazine nitrogen in pure hydrazine sulfate and then in semicarbazide hydrochloride. The hydrazine nitrogen in the following semicarbazones was determined by the unmodified Jamieson procedure: acetophenone semicarbazone, cyclohexanone semicarbazone, diethyl ketone semicarbazone, and acetone semicarbazone. This procedure was applicable also to semicarbazide hydrochloride. In the cases of the semicarbazones of

benzylphenone, benzaldehyde, and cinnamic aldehyde it was necessary to heat the hydrochloric acid solution to 100° C. in order to hydrolyze the semicarbazones.

Furfural semicarbazone was treated by both procedures described above, but on titration with the solution of potassium iodate no end point was reached. The hydrazine nitrogen in thiosemicarbazide could not be determined by the Jamieson technique. Hydrolysis was attempted by employing a 10 per cent solution of sodium hydroxide, digestion with concentrated sulfuric acid, and lastly evaporation to dryness from a concentrated solution of hydrochloric acid. In the last method values were obtained which corresponded to twice those expected.

*p*-Bromophenylhydrazine hydrochloride gave the following results:

Weight of sample taken: 0.0296, 0.0311, 0.0482 gram  
Found: 0.0302, 0.0309, 0.0476, gram; % error, +2.0, -0.6, -1.2

Dextrose and lactose phenylosazones were analyzed by the Jamieson method and consistent values were obtained but they were between the values which would be expected if (1) one phenylhydrazine molecule had reacted and (2) two phenylhydrazine molecules had reacted with one molecule of the sugar. These results are not understood.

## Conclusion

This work has demonstrated that the Jamieson method for hydrazine is applicable to the determination of hydrazine nitrogen in semicarbazide and the semicarbazones of a number of aldehydes and ketones. The method failed in the case of furfural semicarbazone. The method is successful for *p*-bromophenylhydrazine but not for thiosemicarbazide. Sugar osazones gave anomalous results.

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ABSTRACT of the thesis presented by Thomas G. Wheat in partial fulfillment of the requirements for the degree of bachelor of science in chemistry in the Polytechnic Institute of Brooklyn, June, 1938



# Colorimetric Determination of Chlorine with *p*-Aminodimethylaniline

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THE American Public Health Association recommends the *o*-tolidine method (2) for the determination of residual chlorine. A more recent colorimetric method is based upon the use of *p*-aminodimethylaniline as the color-forming reagent. Important papers dealing with the latter procedure are those of Kolthoff (7), Alfthan and Jarvis (1), and Haase and Gad (5).

Since a spectrophotometric study had revealed interesting facts concerning the *o*-tolidine method (4), it seemed worth while to investigate the *p*-aminodimethylaniline method in a similar manner. This paper presents a summary of what were considered the most significant results obtained. After a preliminary investigation of the earlier proposals for applying the method, the work was finally confined to the more promising modification of Haase and Gad.

## Experimental Work

**APPARATUS AND REAGENTS.** The general technique followed, including the preparation and handling of standard solutions of chlorine, was reported previously (4). Most of the color measurements were made with a recording spectrophotometer, set for a spectral band width of 10  $\mu$ , and the pH values were determined with a glass electrode.

The reagent was prepared by dissolving 0.10 gram of *p*-aminodimethylaniline hydrochloride (E. K. No. 492) in 10 ml. of water, to which were added first 25 ml. of 85 per cent orthophosphoric acid and then 15 ml. of water containing 1 gram of iron-free sodium dihydrogen phosphate dodecahydrate. This reagent showed no deterioration in 6 weeks. It was used by adding 0.40 ml. to 100 ml. of sample containing chlorine. Standard comparison solutions were made by diluting to 100 ml. the required volumes of an acidified solution of methyl red prepared according to the directions of Alfthan and Jarvis (1) except for making the concentration 0.00161 per cent.

**THE COLOR REACTION.** When the reagent is added to a dilute solution of chlorine, a purple hue develops. Presumably the color may be attributed to a meriquinone (3, 9, 11), known as Wurster's red, formed by the oxidizing action of chlorine on *p*-aminodimethylaniline. Excess chlorine decreases the color, probably through the formation of some quinone. Optimum color development for concentrations of chlorine up to 1.6 p. p. m. were obtained with 0.40 ml. of the reagent. The color developed immediately with chlorine in solution as such, but with chloramine 6 to 7 minutes were required for full color development. Although the colored system is not as stable as one would wish, making comparisons within 5 minutes after development of the color keeps the error from this source within the limit of visual matching errors. Beer's law was found not to hold for concentrations greater than 0.65 p. p. m.

Previous workers specified a pH range of 2.6 to 3.4 (1, 7). The optimum range found is 2.6 to 3.4 for concentrations up to 0.6 p. p. m. and 3.2 to 4.5 for higher concentrations. A change in hue from purple to yellow occurs in the range pH 8 to 9.

Figure 1 (solid curves) shows spectral transmission curves, for a cell thickness of 5 cm., for concentrations from 0.05 to 1.00 p. p. m. As the curves for 0.40, 0.60, and 1.00 p. p. m. were calculated from measurements for 1-cm. cells, they are probably not as reliable as the others. The small band at 530  $\mu$  and the general symmetry of the curves are rather exceptional. The meriquinone system has a true purple hue.

**COLORIMETRIC STANDARDS:** As it is necessary, in using this method with the standard series or comparator technique, to employ permanent standards, the acidified methyl red solution previously recommended (1, 5) was studied. A 0.00161 per cent solution was finally selected. One milliliter of it, when diluted to 100 ml. in a Nessler tube, is colorimetrically equivalent to 0.10 p. p. m. of chlorine, treated with an excess of *p*-aminodimethylaniline, in a sample of 100 ml. The selection of this concentration was based upon the purity and brightness values calculated for I. C. I. illuminant C from the curves in Figure 1 (6, 10). Visually the match between the unknowns and standards is satisfactory, although the respective transmission curves do not check closely. Subsequent work in this laboratory indicates (8) the possibility of using as a standard a solution of potassium permanganate containing excess periodate. However, the methyl red

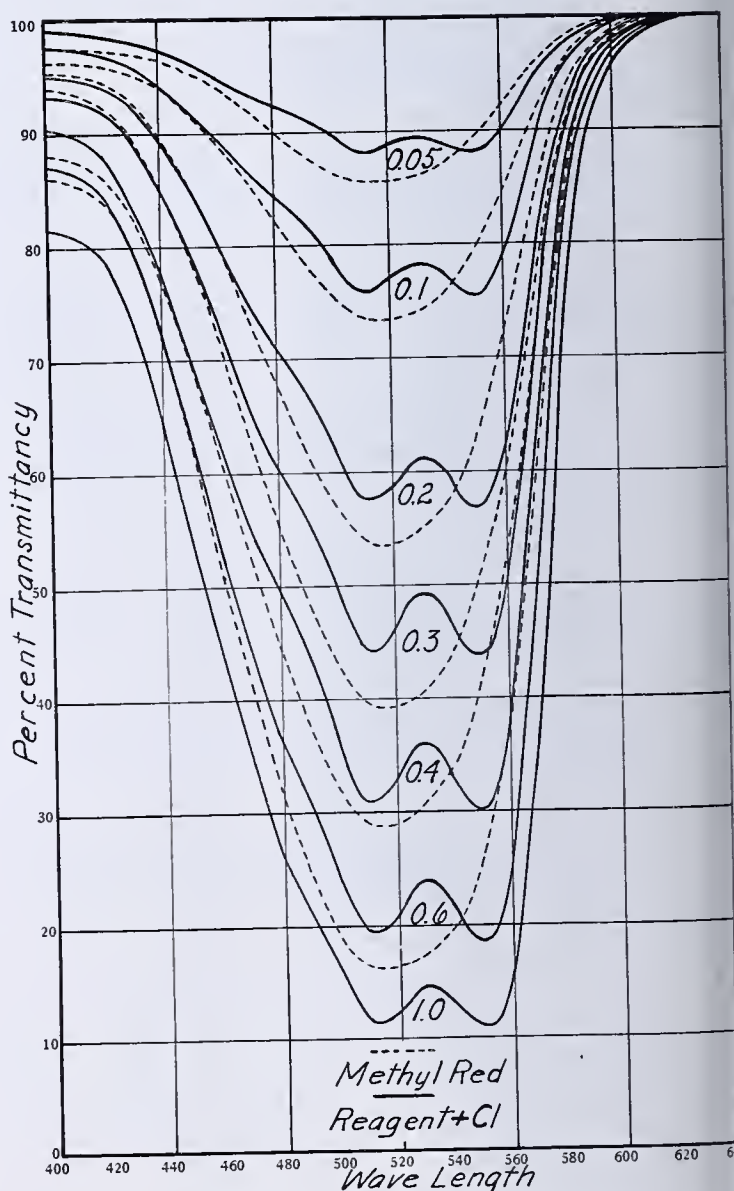


FIGURE 1. SPECTRAL TRANSMISSION CURVES  
Solutions of chlorine plus *p*-aminodimethylaniline (solid curves) and for corresponding methyl red standards (broken curves)



standards were stable for several weeks and conform closely to Beer's law over the range used.

**INTERFERING IONS.** Since the color reaction rests on the oxidizing capacity of chlorine, interference may be expected with certain substances, such as the ferric and nitrite ions, just as with the *o*-tolidine method.

Iron increases the color intensity. For free chlorine the error for 0.1 p. p. m. of iron is equivalent to about 0.01 p. p. m. of chlorine. This error is doubled for 1.0 p. p. m. of iron. As the iron interference, at least at the beginning, is a function of time, larger errors may be expected with the slower acting chloramine. In this case, in the normal course of a determination, 0.1 p. p. m. of ferric iron will interfere to the extent of 0.02 p. p. m. of chlorine. Nitrites decrease the color intensity, the error being approximately of the same magnitude as that for iron. Chloramine gives a larger error than free chlorine.

### Summary

A spectrophotometric study of the *p*-aminodimethylaniline method for the colorimetric determination of residual chlorine has shown the characteristics of the colored system and confirmed reports of others on certain factors affecting the appli-

cation of the method. A change in concentration of the methyl red solution for standards is recommended. The sensitivity varies from 0.01 p. p. m. at the lower limit to 0.03 at the higher concentrations. This method seems to have no advantage over the more familiar *o*-tolidine method unless one prefers matching purple rather than yellow hues.

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ABSTRACTED from a thesis presented by D. H. Byers to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of master of science.

# Separation of Wood Extractives into Simpler Components

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WOOD is not uniform—that is, it is not chemically or structurally homogeneous. Its composition varies among species, in individual trees, and within the tree itself. In recent years, methods have been developed whereby wood can be quantitatively separated into its three major components: extractives, holocellulose, and lignin. Means for separating the carbohydrate fraction, holocellulose, into simpler components have been described elsewhere (4). Lignin, although amorphous, is relatively homogeneous when prepared from extractive-free wood taken from a single species. The extractive fraction contains by far the greatest variety of compounds. It is with the isolation, estimation, and characterization of the numerous components of this wood fraction that this paper deals.

Extractives are those substances which are removed from plant materials by inert solvents such as ether, alcohol, and water. They are not an organic part of the structural elements or of the wood substance. Materials removed from wood by the use of chemical reagents, such as alkalies, mineral acids, and bleaching agents, lie outside of the above definition, for these reagents attack the wood substance and remove portions of the holocellulose and the lignin. It is extremely important to remove the extractives completely before subsequent analysis of the wood is undertaken.

An approach to the separation of the extractives into simpler components may be based on the physical properties of the substances present, such as (1) volatility with steam, (2) solubility in ether, (3) solubility in alcohol, and (4) solubility in water.

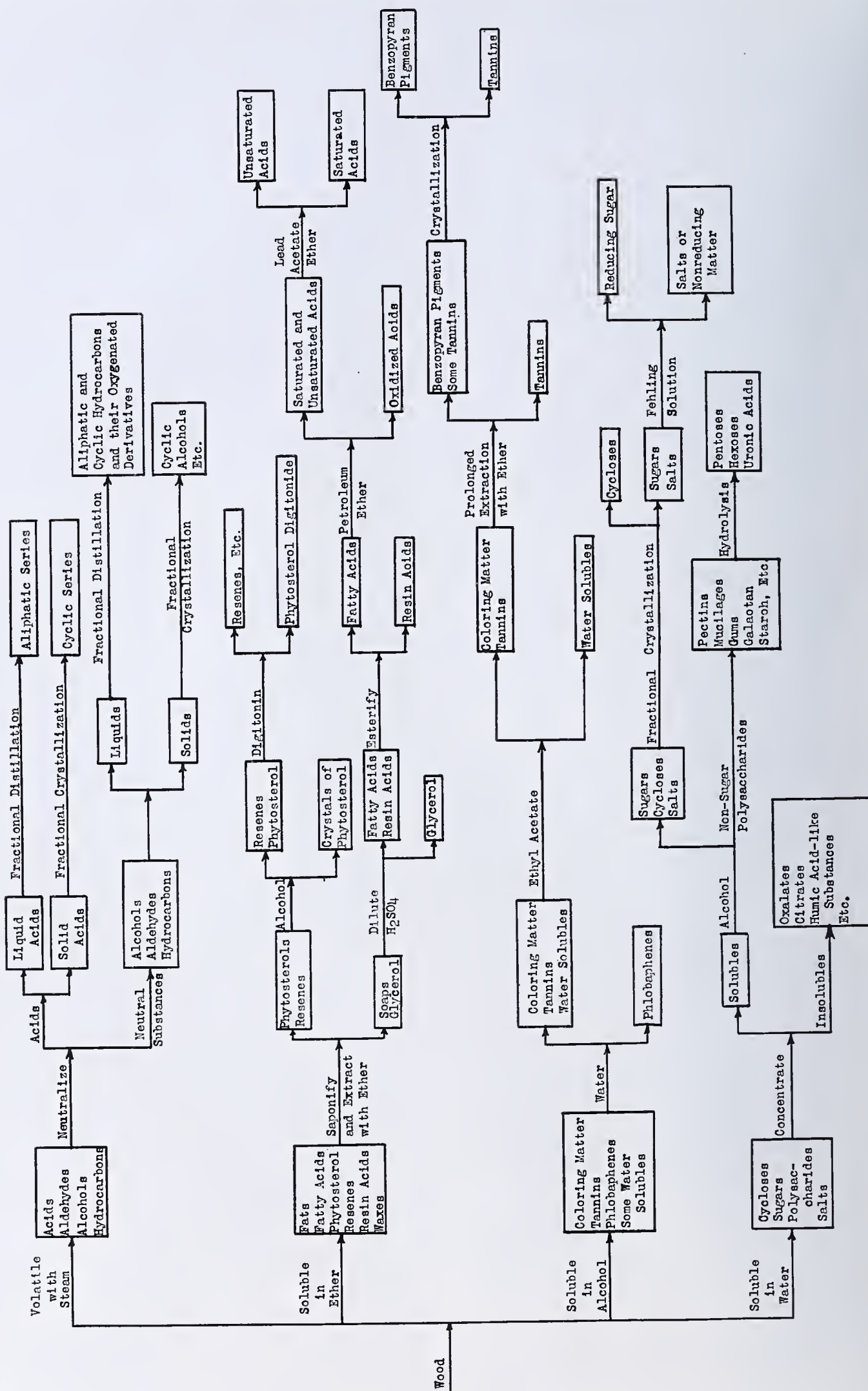
Included in Group 1 are the volatile oils, acids, and hydrocarbons. Representative of this group are alpha- and beta-pinene in the southern pines, dehydroperillic acid and cedrol in western red cedar, and *n*-heptane in Jeffrey and Digger

pinus. Group 2 contains the materials in Group 1 that have not been removed previously by steam distillation and, in addition, the fats, fatty acids, resin acids, resenes, sterols, waxes, and nonvolatile hydrocarbons. All the above classes of substances are present in the *Pinaceae*. Group 3 contains materials in Groups 1 and 2 that have not been removed previously and, in addition, the tannins, phlobaphenes, and the natural pigments. Group 4, after extractions have been successively made with ether and alcohol, includes the soluble carbohydrates, cyclases, and salts.

The separation into the above groups is based on the assumption that the wood has been air-dried and ground to pass a 40-mesh screen. The ether-soluble material may be removed by 8 hours' continuous extraction in a Soxhlet type of extractor. Prolonged treatment with ether is to be discouraged, for in such instances some of the natural pigments related to the phlobatannins will be dissolved. Substitution of petroleum ether or chloroform for the ether leaves these pigments undissolved.

Extraction of the tannins, phlobaphenes, and related pigments, when a further investigation is desired, is preferably done with alcohol at room temperature. With wood containing a large amount of tannin and phlobaphene, it is sometimes necessary to remove the last traces of these substances by extraction with hot alcohol acidified with approximately 3 per cent of acetic acid. The difficulty of removing all the tannin and phlobaphene, particularly from old heartwood, stumpage, and roots, is due to the reaction of these substances with the mineral salts in the soil water to form insoluble salts. Treatment with acidified alcohol decomposes these salts and renders the tannin and phlobaphene soluble. Since the phlobatannins are related to the benzopyran pigments, they are capable of acting as indicators and they give







characteristic colorations with dilute alkalis. Testing the alcohol-extracted wood with a dilute solution of sodium carbonate will reveal whether or not the phlobatannins have been completely removed.

Extraction of the fourth group of materials is carried out with hot water following the treatment with ether and alcohol.

A further separation and estimation of the amounts of each component in the above groups may be made as follows:

### Materials Volatile with Steam

Substances in this group are largely absent in broad-leaved trees or dicotyledons, but they occur in limited amounts in the xylem of softwoods or conifers. Exceptions may be found, however. Nonacidic materials are separated from the acidic materials by neutralization with dilute alkali followed by extraction with ether. Further separation into the individual components is performed by fractional distillation in the case of the liquids and by fractional crystallization in the case of the solids.

### Materials Soluble in Ether

Saponification of the ether extract with alcoholic potassium hydroxide, followed by extraction of the mixture with ether, separates most of the neutral from the acidic components. The hydrocarbons, resenes, glycerol, phytosterols, and such alcohols as were part of the waxes will be present as unsaponifiable matter. In the case of the extractive from pine sapwood, this fraction will be largely phytosterol (3). Treatment of the unsaponifiable fraction with digitonin precipitates the sterols as digitonides (1). Usually a satisfactory separation of the components of the neutral fraction can be accomplished by fractional crystallization from hot alcohol.

The soap residue from the neutral fraction upon acidification and extraction with ether gives the free fatty and resin acids. Glycerol, as it is readily soluble in water and insoluble in ether, will be retained in the aqueous solution from these acids.

A quantitative separation of the resin acids from the fatty acids is accomplished by preferential esterification of the fatty acids with absolute alcohol in the presence of sulfuric acid (6). Separation is then readily effected by transforming the resin acids into their water-soluble sodium salts with sodium hydroxide solution, and extracting the esters of the fatty acids with ether.

After saponification of the esters and precipitation of the acidized acids with petroleum ether, the saturated fatty acids may be separated from the unsaturated fatty acids by the acid salt-ether method (2). The percentage of oleic and stearic acids in the mixture can be calculated from the iodine value.

### Materials Soluble in Alcohol

Extraction of the ether-extracted wood residue with alcohol removes the tannin, phlobaphenes, and associated coloring matters. Most tannins occurring in wood belong to the phlobatannin class, in contrast to the depside class, such as galotannin, penta-*m*-digalloylglucose, which occurs in gallnuts. It has long been held that the phlobatannins are related to the benzopyran pigments—e. g., fisetin, catechin, quercetin, and quercetin, with which they naturally occur. These pigments are crystalline and, since they give the same reactions and the same phenolic degradation products, they are easily converted to amorphous tanninlike materials, and are said to be the precursors of the phlobatannins.

Occurring with the phlobatannins and the benzopyran

coloring matters are the phlobaphenes. They may be derived from the phlobatannins by any process which causes dehydration. Russell (5) has demonstrated that the phlobatannins are in reality hydroxyflavopinacols. Phlobaphenes are insoluble in water, whereas the benzopyran pigments and the phlobatannins are soluble. This fact is made use of in their separation. The alcohol is thoroughly removed from the extract by evaporation or by steam distillation and replaced with water. The insoluble phlobaphene separates as a colloidal dark-colored precipitate which, after drying, changes to a red amorphous powder.

Tannin and coloring matter in the aqueous solution from the phlobaphene precipitation are isolated by extraction with ethyl acetate. The amount of crystalline pigment occurring with the tannin is usually very small. Isolation and identification of the crystalline coloring matter are generally accomplished by prolonged extraction of the concentrated tannin extract with ether. Evaporation of the ether leaves the coloring matter in the form of impure crystals, which are then purified by recrystallization from alcohol or alcohol-benzene mixture.

In some instances, the aqueous solution from the ethyl acetate extraction of the phlobatannin and pigments will contain a small amount of additional materials, generally of the same nature as those substances present in Group 4. As the tannins are very susceptible to the action of heat and air, a tannin fraction, which is insoluble in ethyl acetate, may remain in the aqueous solution. This fraction may be readily separated from the other water-solubles by evaporating the solution to semidryness and then dissolving with acetone.

### Materials Soluble in Water

The aqueous extract from the ether- and alcohol-extracted wood residue contains a mixture of miscellaneous substances, the nature of which depends to a large extent upon the species of wood under investigation. This group includes salts, sugars, cycloses, and such nonsugar polysaccharides as gums, mucilages, starch, pectinlike materials, and galactans. Seldom do all these materials occur in one extract.

Upon concentration of the extract by distillation *in vacuo*, the major portion of the more insoluble salts separates from solution and is filtered off. The nonsugar polysaccharides separate as colloidal precipitates when the concentrated extract is poured into five volumes of alcohol. The cycloses, when present, slowly separate as crystals in the alcoholic filtrate from the polysaccharide precipitation after standing 24 to 48 hours. The percentage of sugars is estimated by a reducing sugar determination. Identification and estimation of the individual sugars in a mixture of one or two sugars can be performed by preparing suitable hydrazones. Where complex sugar mixtures are obtained—e. g., glucose, galactose, mannose, arabinose, and xylose—these can be successfully determined through selective fermentations (4).

The cycloses occur in some softwoods and hardwoods. Both pinite and sequoyite are found in redwood, and pinite is also found in sugar pine. *i*-Inositol occurs in ash and oak.

The scheme of separation is summarized in the diagram.

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# Factors Influencing the Quantitative Determination of Sulfate as Barium Sulfate

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ALMOST the entire history of barium sulfate precipitates is marked by references to annoying, unexplained, and often uninvestigated interference by common substances, the presence of which might be expected from theoretical considerations to produce little or no interference. Of these one of the commonest and most troublesome has been the nitrate ion, usually present with the alkali elements (20, 27). The phenomenon has been variously blamed on adsorption, coprecipitation, occlusion (23), and the formation of various types of unisolated, insoluble complex-compounds (4).

Quantitative results based on the weight of precipitate range from slightly low to several per cent greater than the amount required by theory. These variations depend upon conditions observed during the formation and treatment of the precipitated material. It seemed desirable, as a basis for further study as well as for the purpose of limiting analytical conditions, to study in more detail the relationship between these errors and the conditions that influence them.

Equal amounts of sulfates were precipitated with an excess of barium chloride solution in the presence of various amounts of salts and acids. Potassium salts were used for the most part, and the results compared under certain conditions with other salts. A standard procedure for the treatment of the precipitate was adopted, and the effect of varying nearly all possible variable factors in this procedure was tested at certain regular intervals. The salts and acids used were of analyzed reagent grade, which were tested for freedom from interfering substances and found to conform in general to A. C. S. standards for reagent grade chemicals.

## General Technique

Where precipitation was conducted above room temperature, the sulfate solution was maintained at that temperature on an electric hot plate. Solutions were stirred mechanically while barium chloride solution was added from a buret at a rate determined by the attachment of a calibrated delivery tip. After the measured volume of precipitant had been added, the stirrer and cover glass were cleaned, and the solution was allowed to stand, either on a steam plate or at room temperature, for a definite length of time. The solution was then decanted through a porcelain filtering crucible, and the filtrate tested for excess of barium ion. The precipitate, after having been washed by decantation, was transferred to the crucible, washed further, and finally dried to constant weight.

This investigation has considered the effect of some twenty different factors that are commonly encountered in the course of an ordinary sulfate determination.

## General Conditions

The behavior of potassium sulfate in the presence of potassium nitrate under different conditions has been studied extensively, and the results have been compared with other sulfates and nitrates. Although the effect of

variation on nearly all conditions was studied at certain points, most conditions have remained fixed throughout the greater part of this investigation. To simplify comparison of the numerical results given, and to reduce the number of conditions that must be listed in connection with each set of figures, the following values apply, except where different values are specifically stated:

The precipitates were not ignited, but were dried to constant weight at 110° to 120° C.

The concentration of sulfate at the start of precipitation was 0.01 molar and the volume was 350 cc.

The concentration given for various salts and acids present is for the initial volume.

Barium chloride solution 0.05 molar at 25° to 30° C. was added to 5 per cent in excess.

Cold precipitation was at 25° to 30° C.; for hot precipitation the initial temperature of the sulfate solution was 95° to 100° C.

The final volume with 5 per cent excess barium chloride was 425 to 430 cc.; with 50 per cent excess, 460 to 465 cc.; and with 100 per cent excess, 495 to 500 cc.

Stirring was always by a motor-driven stirrer at uniform rate of speed.

Hot digestion was at the temperature maintained by a steam heated plate, at 80° to 85° C.

Wash water was 200 to 300 cc. of distilled water at 25° to 30° C.

The sulfate used for precipitation was in each case theoretically equivalent to 0.8166 ( $\pm 0.0002$ ) gram of barium sulfate. Each result quoted in the following tables should theoretically have been 0.8166 gram. The difference in each case represents the error.

## Experimental Investigation of Factors

CONCENTRATION OF SULFATE ION IN SOLUTION. The figure given in Table I show the weight of barium sulfate obtained from equal weights of potassium sulfate at different concentrations, under the conditions indicated. Variations in the

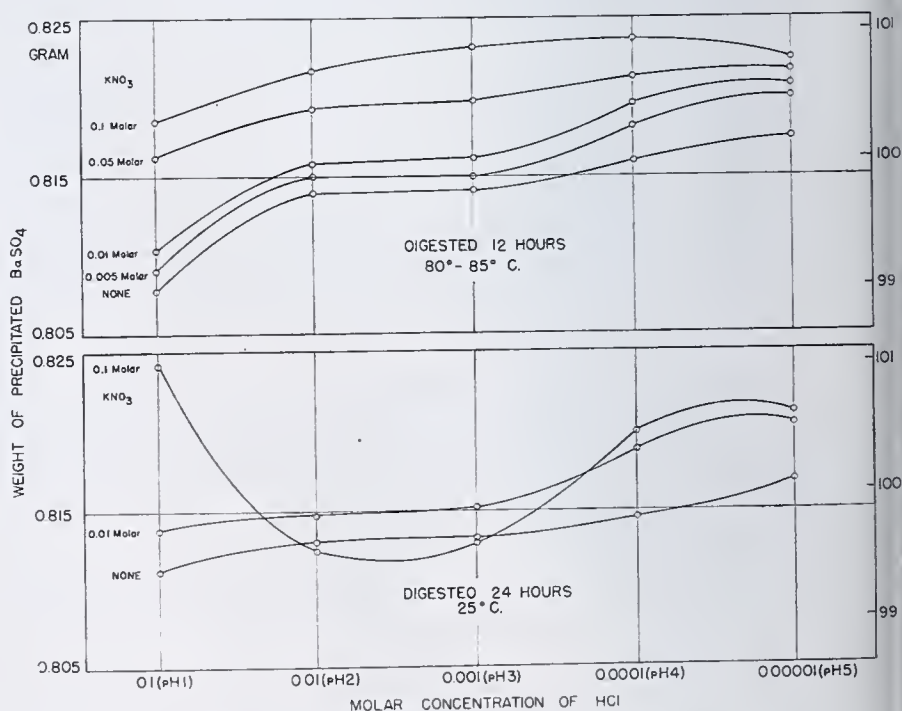


FIGURE 1. EFFECT OF HOT AND COLD DIGESTION

Unignited precipitate obtained by adding 0.05 molar  $\text{BaCl}_2$  to 5 per cent in excess in 5 minutes to hot (95° to 100° C.) 0.01 molar  $\text{K}_2\text{SO}_4$  solution of varying concentration with respect to  $\text{HCl}$  and  $\text{KNO}_3$ .

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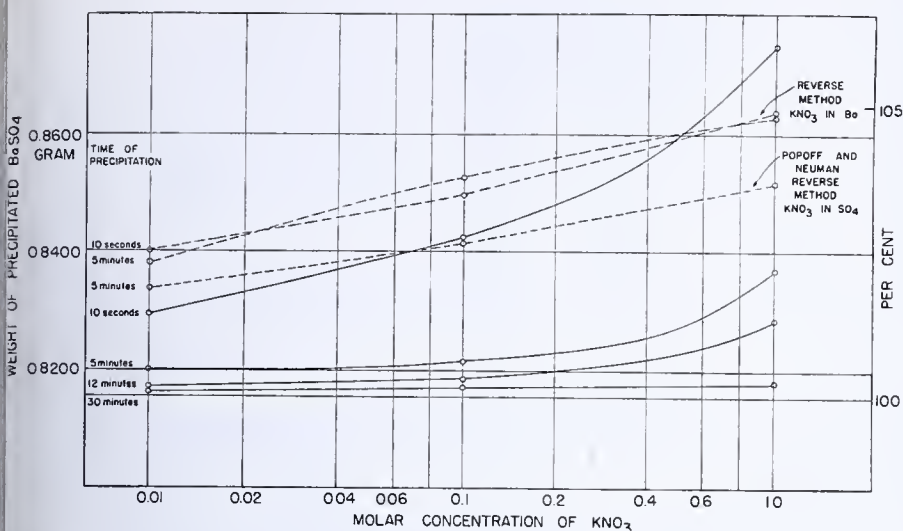


FIGURE 2. COMPARISON OF REVERSE AND REGULAR PRECIPITATION METHODS

Ignited precipitate obtained by adding 0.05 molar  $\text{BaCl}_2$  to 5 per cent in excess to hot (95° to 100° C.) 0.01 molar  $\text{K}_2\text{SO}_4$  at different rates, where sulfate solution is of varying concentration with respect to  $\text{KNO}_3$  (solid lines), compared with results (broken lines) obtained by adding same weight of  $\text{K}_2\text{SO}_4$  to hot  $\text{BaCl}_2$  solution. No acid added except in the Popoff and Neuman determination.

concentration of potassium sulfate between 0.005 and 0.02 molar produced differences of less than  $\pm 0.5$  mg. in 815 gram of the precipitate if no potassium nitrate was present.

**CONCENTRATION OF POTASSIUM NITRATE PRESENT.** The effect of nitrates upon the weight of barium sulfate precipitates has been shown to be a function of the concentration of the nitrate (4), at least up to a certain point (1).

TABLE I. EFFECT OF VARYING CONCENTRATION OF SULFATE  
Same weight of  $\text{K}_2\text{SO}_4$ . 0.01 molar  $\text{KNO}_3$ , 0.01 molar  $\text{HCl}$ ,  $\text{BaSO}_4$  precipitated hot (95° C.) in 5 minutes by  $\text{BaCl}_2$  to 5 per cent excess. Digested 12 hours hot]

0.005 Molar $\text{K}_2\text{SO}_4$ Gram	0.01 Molar $\text{K}_2\text{SO}_4$ Gram	0.02 Molar $\text{K}_2\text{SO}_4$ Gram
0.8141	0.8153	0.8161

The effect of potassium nitrate has been studied where the concentrations at the start of the precipitation were 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0 molar. The effect of these concentrations upon the weight of the precipitate of barium sulfate is shown in Figures 1 to 4. (For the sake of brevity, only graphic data are given in some instances. For the numerical data the reader is referred to the original thesis.)

**CONCENTRATION OF HYDROGEN ION IN SOLUTION.** Sufficient hydrochloric acid was used to render the solution at the start of precipitation 0.1, 0.01, 0.001, 0.0001, or 0.00001 molar with respect to hydrochloric acid. These concentrations are equivalent to pH values of approximately 1, 2, 3, 4, and 5, respectively, for the initial volume of 350 cc. of water in which the potassium sulfate and potassium nitrate are dissolved and in which the barium chloride solution is added during the precipitation.

The curves (Figure 1) for hot and cold digestion differ in some cases, but are nearly parallel to the base line between 0.01 and 0.001 molar hydrochloric acid for concentrations of 0.01 molar potassium nitrate. In the case of hot digestion, all values lie within 3 parts per 1000 of the theoretical value required. The solution, then, should not be more than 0.01 molar with respect to nitrate and should be made from 0.01 to 0.001 molar with respect to hydrochloric acid (pH 2 to 3), preferably nearer 0.01 molar.

The sulfate is precipitated from hot solution in about 5 minutes and digested hot for 12 hours. If the solution is digested cold for 24 hours, the effect of larger concentrations

of potassium nitrate is less between 0.01 and 0.001 molar hydrochloric acid, but all results then carry a negative error of 2 to 3 parts per 1000.

**KIND OF BARIUM SALT USED AS PRECIPITANT.** Barium chloride was used throughout and always at room temperature. No other salt or acid was added to the barium chloride solution except in a few cases of reverse precipitation (Table IV). The results in these cases are abnormally high.

**CONCENTRATION OF BARIUM SOLUTION.** Barium chloride 0.05 molar was used in this investigation, and was compared under the conditions shown in Table II with 0.1 and 0.5 molar solutions. The latter solution gave slightly higher results in the presence of nitrates.

**TEMPERATURE OF SOLUTION DURING PRECIPITATION.** Temperatures were taken at the start of, rather than during, precipitation. The beaker was heated over a gas burner, then transferred to a small electric hot plate during precipitation. This plate furnished sufficient heat to keep the solution at the boiling temperature with slow ebullition.

TABLE II. CONCENTRATION OF BARIUM CHLORIDE SOLUTION  
( $\text{BaSO}_4$  precipitated hot in 5 minutes by  $\text{BaCl}_2$  to 5 per cent excess. Digested 12 hours hot)

$\text{KNO}_3$ Molarity	$\text{HCl}$ Molarity	Barium Sulfate Precipitated		
		0.05 molar $\text{BaCl}_2$ Gram	0.1 molar $\text{BaCl}_2$ Gram	0.5 molar $\text{BaCl}_2$ Gram
None	0.01	0.8142	0.8148	0.8146
0.01	0.01	0.8153	0.8161	0.8194
0.1	0.01	0.8211	0.8211	0.8239

Since the barium chloride was always used at room temperature, the heater did not entirely counteract the cooling effect of the added barium chloride in the more rapid additions (10 seconds, 1 minute, 2 minutes). Here the drop in temperature was less than 15° C. for boiling hot solutions. For additions in 5 minutes' time, the cooling effect was less than 5° C., and for slower additions (12 and 30 minutes) it was practically canceled. In precipitations made at room temperature, this effect is absent. For precipitations at intermediate temperatures (45°, 60°, and 75° C.), heat from the hot plate was supplied during precipitation, and the temperature was kept within  $\pm 5^\circ$  of the value given. Where 50 or 100 per cent excess barium chloride was added at the end of precipitation time stated, the solution was cooled further as a result.

TABLE III. EFFECT OF TEMPERATURE OF SULFATE SOLUTION DURING PRECIPITATION

( $\text{BaSO}_4$  precipitated by 0.05 molar  $\text{BaCl}_2$  to 5 per cent excess, in 5 minutes)

$\text{KNO}_3$ Molarity	$\text{HCl}$ Molarity	25° to 30° C. Gram	40° C. Gram	55° to 65° C. Gram	75° C. Gram	95° to 100° C. Gram
		Digested 12 Hours Hot				
0.01	0.01	0.8277	....	0.8197	....	0.8153
Digested 24 Hours Cold						
0.1	0.01	....	0.8456	....	0.8187	0.8118
0.01	None	0.8402	0.8329	0.8261	0.8223	0.8201
0.1	None	0.8710	0.8504	0.8360	0.8300	0.8203

The effect of temperature may be seen in Figures 3 and 4.

Cold precipitation (25° C.) increases errors of contamination somewhat in all cases (2, 17, 25), but much more where the addition of barium chloride is rapid (22), where the excess of barium chloride added is large, or where the concentration of nitrate is high. It is necessary to precipitate barium sulfate near the boiling point if these errors are to be reduced to a minimum.



TABLE IV. REGULAR AND REVERSE PRECIPITATION

Conditions	Precipitation Min.	HCl Molarity	No KNO <sub>3</sub> Gram	0.01 Molar KNO <sub>3</sub> Gram	0.1 Molar KNO <sub>3</sub> Gram	0.354 Gram KNO <sub>3</sub> Gram	0.01 Molar KNO <sub>3</sub> , No HCl Gram	1.0 Molar KNO <sub>3</sub> Gram
BaCl <sub>2</sub> added to K <sub>2</sub> SO <sub>4</sub> , KNO <sub>3</sub> in K <sub>2</sub> SO <sub>4</sub>	5	0.01	0.8141	0.8153	0.8213	0.8153	0.8204	....
Popoff and Neuman reverse method: Dried at 115° C.	5	0.03	0.8190	0.8338	0.8423	0.8372	0.8346	0.8521
Ignited 1 hour at 600–700° C.	5	0.03	0.8165	0.8273	0.8335	0.8303	0.8271	0.8425
K <sub>2</sub> SO <sub>4</sub> added to BaCl <sub>2</sub> , KNO <sub>3</sub> in BaCl <sub>2</sub>	10 seconds hot	None	0.8242	0.8404	0.8490	....	....	0.8639
	5 minutes hot	None	0.8170	0.8386	0.8525	....	....	0.8636

**MANNER OF ADDITION OR MIXING.** The usual procedure in sulfate determination has been to add the barium solution to the sulfate solution. In the "reverse" method recommended by Popoff and Neuman (21) the sulfate solution is added to the barium solution. Figure 2 compares this method with the "regular" precipitation method. The chloride contamination is much higher in the case of reverse precipitation (1, 22).

The broken lines indicate the results of reverse precipitation in 10 seconds and in 5 minutes with potassium nitrate present in the barium chloride solution, in comparison with the Popoff and Neuman method where the potassium nitrate is in the sulfate solution and the barium chloride solution is made 0.03 molar with respect to hydrochloric acid. The solid lines show the results of the usual type of precipitation where barium chloride is added to the potassium sulfate solution containing potassium nitrate but no acid. The reverse method is more susceptible to contamination by nitrate at low concentration than is the regular method (28, 30); consequently this regular method has been adhered to elsewhere in this investigation. All these precipitations were made from the hot solution.

**RATE OF ADDITION OF BARIUM SOLUTION.** In the past this factor has been the subject of much attention and nearly as much disagreement among analysts (1, 13, 18, 19, 24). While undoubtedly the errors due to rapid addition will occasionally cancel out other errors and give the theoretical results desired, it is almost certain to be the wrong technique in the large majority of cases, especially where any nitrate is present.

In this investigation the barium chloride solution was added from a buret having interchangeable glass tips, calibrated to deliver in the desired length of time the theoretical amount of the solution required plus 5 per cent in excess.

The relation of precipitation rate to the weight of precipitate formed is shown in Figures 3 and 4 in connection with different temperatures and different concentrations of potassium nitrate. Values for addition of the precipitant in 10 seconds, and 1, 5, 12, and 30 minutes are shown. Sudden addition in 2 or 3 seconds gave erratic results.

**RATE OF STIRRING DURING PRECIPITATION.** A motor stirrer was used. This mechanical stirring was compared in a few experiments with hand stirring in which a straight glass rod was used. The results show no difference within the experimental error.

**EXCESS OF BARIUM SOLUTION ADDED.** The variation of this value explains to some extent the erratic results heretofore obtained when nitrates were present in sulfate samples (4, 7, 11, 25). For precipitates formed slowly in the absence of nitrates and hydrochloric acid, the excess of barium chloride added has no effect upon the weight of dry precipitate. Excesses of 50 or 100 per cent, if added after rapid precipitation at room temperature in the absence of potassium nitrate and hydrochloric acid, give slight increases of 2 and 4 mg. in 816 mg. (22). In the presence of increasing concentrations of potassium nitrate this effect increases greatly, being augmented always by conditions of rapid or cold precipitation until, for molar potassium nitrate, it produces a 50-mg. increase in weight of precipitate, over 6 per cent of the theoretical value.

The excess of precipitant above 5 per cent was added all at once, immediately after the timed addition of the first 10 per cent of barium chloride.

Figure 4 shows the effect of excess of barium chloride at different precipitation rates, for different temperatures, and in the presence of different concentrations of potassium nitrate. If the precipitate is formed in a solution acid with hydrochloric acid and is then subjected to hot digestion,

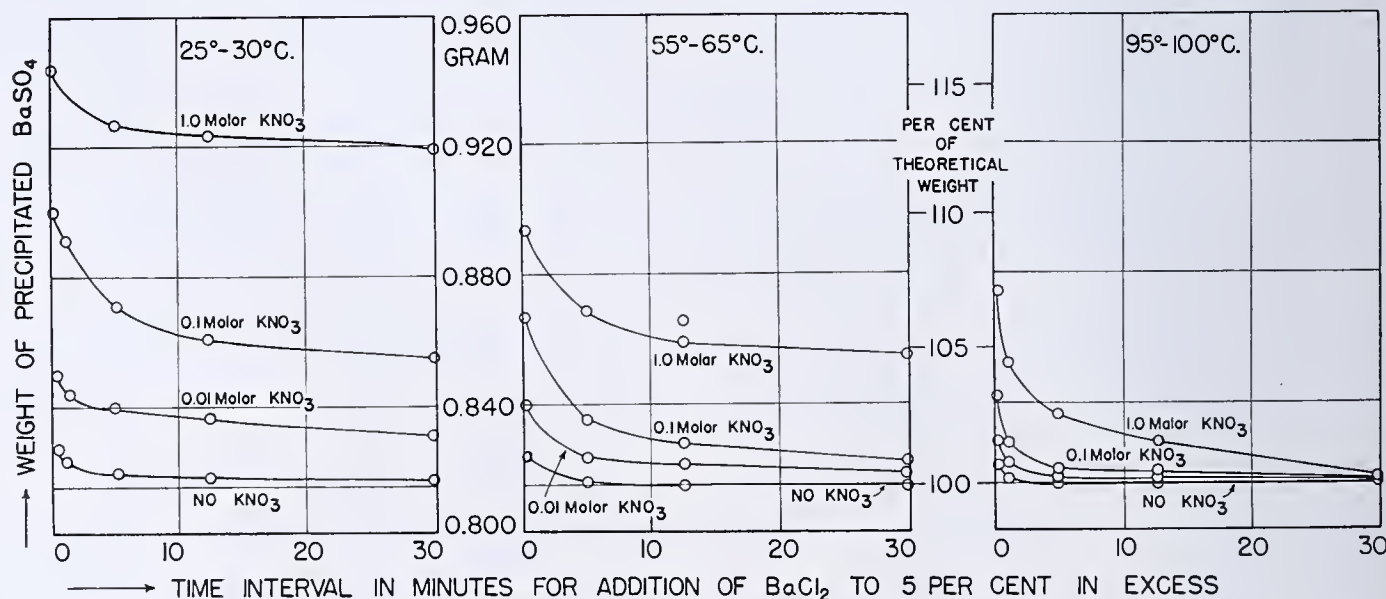


FIGURE 3. EFFECT OF TIME INTERVAL

Unignited precipitate obtained by adding 0.05 molar BaCl<sub>2</sub> to 5 per cent in excess at different rates to 350 cc. of unacidified 0.01 molar K<sub>2</sub>SO<sub>4</sub> made 0.00, 0.01, 0.1, and 1.0 molar with respect to KNO<sub>3</sub>. Temperature of sulfate solution at start of precipitation, 25° to 30° C., 55° to 65°, or 95° to 100° C. Precipitates digested 24 hours at 25° C.



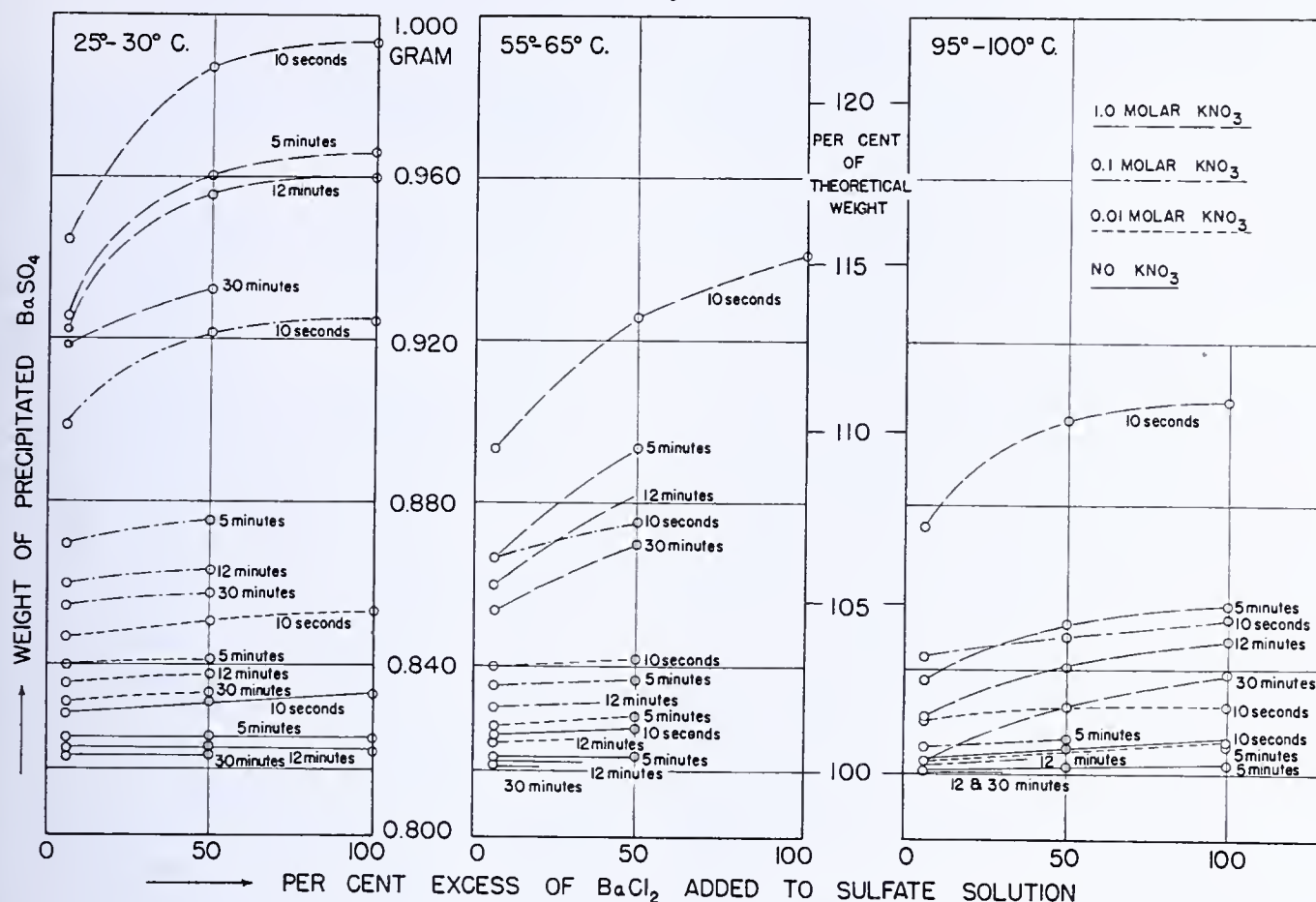


FIGURE 4. EFFECT OF EXCESS BARIUM CHLORIDE

Unignited precipitate obtained by adding 5, 50, and 100 per cent excess of 0.05 molar  $\text{BaCl}_2$  to 350 cc. of unacidified 0.01 molar  $\text{K}_2\text{SO}_4$ , made 0.00, 0.01, 0.1, and 1.0 molar with respect to  $\text{KNO}_3$ , where first 105 per cent of  $\text{BaCl}_2$  was added in 10 seconds and 5, 12, and 30 minutes. Temperature of sulfate solution at start of precipitation was 25° to 30°, 55° to 65°, or 95° to 100° C. Precipitates digested 24 hours at 25° C.

ger excess of barium chloride produces slightly lower results.

**TEMPERATURE DURING DIGESTION.** Digestions were conducted at room temperature or on a steam plate which maintained the solutions at a temperature of approximately 80° to 85° C.

Hot digestion removes more of the impurities from the precipitate and does so more rapidly than cold digestion. The difference is, of course, greater for greater contamination. The temperature of the supernatant liquid also affects the solubility of the barium sulfate in it. No correction was made for this slight error.

The results of hot and cold digestion are compared with length of digestion and other factors in Table V and in Figure 1.

**DIGESTION TIME.** Table V shows that under some conditions the length of this interval exerts a considerable influence upon the weight of precipitate obtained. This difference may amount to more than 5 per cent of the weight of the contaminated barium sulfate precipitated rapidly from cold unacidified solutions in the presence of a large amount of potassium nitrate. Weight is also influenced to a considerable extent by the concentration of hydrochloric acid present. The change in the precipitate during hot digestion is a loss of weight due to contaminating substances passing from the precipitate into the solution. Several per cent of potassium nitrate along with traces of chloride have been leached from such precipitates.

During the early part of the digestion period a gain in weight of precipitate is also taking place, due to the overlapping of the precipitation period, caused by temporary supersaturation of the solution with respect to barium sulfate.

Another type of delayed precipitation, of much longer duration, was observed in the case of precipitates obtained from solutions of molar potassium nitrate. Here gains in weight up to 35 mg. (out of more than 900 mg. of precipitate) occurred upon standing 48 hours, with additional gains of as much as 10 mg. beyond that point. This occurs in varying degrees whether the precipitates are formed in hot or cold solution, whether the barium chloride is added rapidly or slowly (10 seconds or 5 minutes), in 5 or 50 per cent excess, but only on cold digestion. This precipitation occurs even in the filtered supernatant liquid when it stands separated from the precipitate already formed. In this case the precipitate (as much as 43 mg.) was barium sulfate contaminated with considerable amounts of potassium and nitrate.

Clearly the phenomenon is related to the cold supernatant liquid, which must retain a considerable quantity of sulfate in solution and allow its slow release to some form from which it can subsequently precipitate.

The facts that much of the precipitate from the separated supernatant liquid forms upon the walls of the beaker, and that the liquid itself appears clear and free from turbidity seem to argue against the idea of the retained material's being suspended in ultramicroscopic crystalline form. The variety of conditions influencing crystal form and size, the complete filterability through fine porous refractory material or closely packed barium sulfate, and the high specific gravity of the precipitated material do not favor a suspension theory, nor does the fact that the precipitate forms a very closely adhering, crystalline frosting upon the beaker.

The observed facts suggest a complex ion or compound in the potassium nitrate solution (3, 6, 12, 15, 26, 29) withholding sulfate from precipitation and slowly releasing it into an ionic



TABLE V. EFFECT OF TEMPERATURE AND LENGTH OF DIGESTION

	Precipitation	Sec.	Digestion	Precipitate Obtained after Digestion				
				0.5-1 hour	6 hours	12 hours	24 hours	48 hours
				Gram	Gram	Gram	Gram	Gram
No HCl Present, BaCl <sub>2</sub> to 5 Per Cent in Excess								
No KNO <sub>3</sub>	Cold	10	Hot	.....	.....	.....	0.8304	.....
			Cold	0.8322	.....	.....	0.8283	0.8270
	Hot	10	Hot	.....	.....	.....	0.8191	.....
			Cold	0.8212	.....	.....	0.8206	0.8194
	Cold	5	Hot	.....	.....	.....	0.8207	.....
			Cold	0.8198	.....	.....	0.8214	0.8209
0.01 molar KNO <sub>3</sub>	Hot	5	Hot	.....	.....	.....	0.8181	.....
			Cold	0.8164	.....	.....	0.8164	0.8169
	Hot	5	Hot	.....	.....	.....	0.8203	.....
			Cold	0.8194	.....	.....	0.8204	0.8211
	Cold	10	Hot	.....	.....	0.8563	0.8576	.....
			Cold	0.9115	.....	.....	0.9016	0.8667
0.1 molar KNO <sub>3</sub>	Hot	10	Hot	.....	.....	.....	0.8277	.....
			Cold	0.8471	.....	.....	0.8428	0.8411
	Cold	5	Hot	.....	.....	.....	0.8417	.....
			Cold	0.8730	.....	.....	0.8710	0.8619
	Hot	5	Hot	.....	.....	.....	0.8226	.....
			Cold	0.8214	.....	.....	0.8206	0.8228
1.0 molar KNO <sub>3</sub>	Cold	10	Hot	.....	0.8307	0.8262	0.8328	0.8326
			Hot	.....	.....	0.8325	.....	.....
	Hot	10	Cold <sup>a</sup>	0.9118	.....	.....	0.9444	0.9607 <sup>a</sup>
				0.9248	.....	.....	0.9493	0.9611
	Hot	10	Hot	.....	0.8339	0.8270	0.8235	0.8257
			Cold	0.8700	.....	.....	0.8790	0.8818
	Hot	5	Hot	.....	0.8378	0.8282	.....	.....
			Cold	.....	.....	.....	0.8375	.....
	Cold	5	Cold	.....	.....	.....	0.8306	0.8357
				0.8214	.....	.....	.....	.....
	Hot	5	BaCl <sub>2</sub> to 50 Per Cent in Excess					.....
			Hot	.....	.....	.....	0.8421	.....
				0.8416	.....	.....	0.8480	0.8484
0.01 Molar HCl, BaCl <sub>2</sub> to 5 Per Cent in Excess								
				4 hours				
No KNO <sub>3</sub>	Hot	5	Hot	.....	0.8140	0.8141	.....	.....
			Cold	0.8126	.....	.....	0.8130	.....
0.01 molar KNO <sub>3</sub>	Hot	5	Hot	.....	.....	0.8151	.....	.....
			Cold	0.8141	.....	.....	0.8144	.....
0.05 molar KNO <sub>3</sub>	Hot	5	Hot	.....	0.8186	0.8198	.....	.....
			Cold	.....	.....	.....	0.8127	.....
0.1 molar KNO <sub>3</sub>	Hot	5	Hot	.....	.....	0.8212	0.8228	.....
			Cold	0.8120	.....	.....	0.8126	0.8138
	Hot	10	Hot	.....	.....	.....	0.8266	.....
			Cold	0.8307	.....	.....	.....	0.8355

<sup>a</sup> Digested cold 168 hours (7 days) = 0.9706 gram.

form capable of being precipitated from solution. In hot solution the complex is largely broken down; the speed of attainment of equilibrium of the reaction



may be greatly increased, so that precipitation of nearly all the sulfate is completed in a short time, or the point of equilibrium may be shifted in the direction to reduce the concentration of the complex sulfate. Another possibility is that the high concentration of nitrate ion by retarding the attainment of equilibrium may prolong the supersaturation period. Other investigators have recorded the retardation of barium sulfate precipitation by certain compounds (14, 15, 26). The effect of length of time of digestion under various conditions is shown in Table V.

**SUPERNATANT LIQUID PRESENT DURING DIGESTION.** When potassium nitrate was added to the supernatant liquid, after precipitation of the barium sulfate, there was no increase in the weight of the precipitate (4), but a loss was observed which was probably due to the increased solubility of barium sulfate in a strong solution of potassium nitrate. This loss was greater for hot solution.

**TIME OF DRYING.** Precipitates were usually dried from 12 to 18 hours. This gave results concordant to 0.2 mg. where the nitrate contamination was small. Some precipitates which were dried only 4 hours lost excessive amounts of weight upon subsequent drying, indicating that the first drying time was

TABLE VI. BARIUM SULFATE PRECIPITATED

(By 0.05 molar BaCl <sub>2</sub> to 5 per cent in excess in 10 seconds)			
KNO <sub>3</sub> Molarity	During precipitation	During digestion	BaSO <sub>4</sub> Precipitated Gram
Temperature during Digestion ° C.			
At 25° C., Digested 24 Hours			
None	None	25	0.8283
None	1.0	25	0.8276
None	1.0	85	0.8150
1.0	0.8 <sup>a</sup>	25	0.9563
At 95° to 100° C., Digested 48 Hours			
None	None	25	0.8184
None	1.0	25	0.8131

<sup>a</sup> Dilution effect of added BaCl<sub>2</sub> solution.

insufficient. A second drying of 6 to 18 hours gave results that were usually 0.0 to 0.2 mg. lower for 800 to 900 mg. of precipitate.

**IGNITION TEMPERATURE.** To test the effect of drying upon precipitates formed under different conditions a number of precipitates were first dried at 115° C., then held at temperatures of 300° ± 5° C. for two 1-hour periods, at 600° ± 15° for two 1-hour periods, and at 800° ± 25° for one hour. In the case of the less contaminated precipitates obtained under optimum conditions of precipitation the losses were small between 115° and 300° C., and much larger at higher temperatures. For the precipitates containing great



TABLE VII. EFFECT OF IGNITION OF WEIGHT OF PRECIPITATES  
(Precipitated in 5 minutes from 610 mg. of K<sub>2</sub>SO<sub>4</sub>, 5 per cent excess barium chloride)

KNO <sub>3</sub>	HCl	Precipitate Dried at 115° C. Mg.	At 300° C.		Weight Lost during Ignition At 600° C.		At 800° C. 1 hr. Mg.	Total		Analysis of Original Precipitate	
			1st hr.	2nd hr.	1st hr.	2nd hr.		Mg.	%	K Mg.	NO <sub>3</sub> Mg.
			Mg.	Mg.	Mg.	Mg.					
Precipitated Hot, Digested Hot for 12 Hours											
None	0.01	814.1	0.8	0.0	2.0	0.5	0.3	3.6	0.45	4.3	0.0
None	0.001	814.1	0.5	0.0	2.2	0.4	0.4	3.5	0.44	..	..
0.01	0.01	815.4	0.9	0.1	2.0	0.4	0.2	3.6	0.45	4.5	1.2
0.01	0.001	816.0	0.8	0.0	2.3	0.3	0.2	3.6	0.45	..	..
0.1	0.01	821.2	3.9	0.2	2.4	0.4	0.1	7.0	0.87	5.9	1.8
0.1	0.001	821.9	3.2	0.2	3.4	0.0	0.2	7.0	0.87	..	..
Precipitated Hot, Digested Cold for 24 Hours											
0.01	0.01	814.4	1.2	0.0	2.8	0.0	0.3	4.3	0.54	..	..
0.1	0.01	812.6	1.0	0.0	4.3	0.0	0.4	5.7	0.71	..	..
0.01	None	820.3	0.4	0.1	2.1	0.0	0.6	3.2	0.40	5.4	3.5
0.1	None	820.5	0.6	0.2	2.3	0.0	0.8	3.8	0.48	5.1	4.0
Precipitated Cold, Digested Cold for 24 Hours											
0.01	None	840.2	1.6	0.2	4.9	0.6	6.7	14.1	1.67	17.1	10.5
0.1	None	871.0	2.9	0.4	4.1	0.3	14.6	22.5	2.55	24.7	19.8
0.1 <sup>a</sup>	None	875.6	3.3	0.4	4.1	0.5	17.0	25.3	2.89	..	..
Precipitated Cold, No Digestion											
0.1	None	873.0	3.6	0.2	4.5	0.9	13.6	22.9	2.62	..	..
Precipitated Cold, Digested Cold for 48 Hours											
0.1	None	861.9	1.9	0.3	3.8	1.2	9.9	17.2	2.00	..	..
<sup>a</sup> 50 per cent excess BaCl <sub>2</sub> .											

<sup>a</sup> 50 per cent excess BaCl<sub>2</sub>.

amounts of contamination (nitrates), the losses were much greater between 115° and 300° C., and in general greater than the others at higher temperatures. The results of these ignition experiments are given in Table VII.

This investigation shows that in general more reliable and more reproducible results may be obtained by drying such contaminated barium sulfate precipitates to constant weight and by igniting them.

**IGNITION TIME.** Precipitates that had been ignited for 1 hour at 300° or 600° C. showed further loss in weight (Table VII) when they were heated at the same temperature for an additional hour (21). The virtual elimination of this variable at another point in favor of drying the barium sulfate rather than igniting it.

TABLE VIII. KINDS OF CATIONS ACCOMPANYING SULFATE  
K<sub>2</sub>SO<sub>4</sub> precipitated by adding BaCl<sub>2</sub> to 5 per cent in excess in 5 minutes. No HCl. Digested 24 hours cold)

NO <sub>3</sub> Molarity	Precipitation	0.01 Molar H <sub>2</sub> SO <sub>4</sub>	0.01 Molar K <sub>2</sub> SO <sub>4</sub>	0.01 Molar Na <sub>2</sub> SO <sub>4</sub>	0.01 Molar (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
		Gram	Gram	Gram	Gram
None	Hot	0.8174	0.8162	0.8171	0.8176
0.01	Hot	0.8143	0.8202	0.8201	0.8212
0.1	Hot	0.8139	0.8204	0.8201	0.8173
0.1	Cold	0.8562	0.8728	0.8731	0.8762
0.01 Molar HCl except in H <sub>2</sub> SO <sub>4</sub> , Digested Hot 12 Hours					
None	Hot	0.8162	0.8142	0.8160	0.8151
0.01	Hot	0.8145	0.8152	0.8151	0.8157

Composition of Unignited Precipitates

Some of the precipitates considered in Table VII were analyzed for potassium and nitrates.

A weighed portion of precipitate was dissolved in about 25 times its weight of 18 molar sulfuric acid, and reprecipitated by pouring it twice and with stirring into about 25 times its volume of water. The filtrate and washings were evaporated to sulfur dioxide fumes, transferred to a platinum crucible, and evaporated to dryness in an air bath. The residue was dissolved in a little water, filtered, dried, and ignited to constant weight with a small amount of ammonium carbonate. The salt was weighed as potassium sulfate and calculated as potassium. This value was checked against an indirect determination of the potassium from the residue as platinum in potassium chloroplatinate. Other portions of these unignited precipitates were decomposed by boiling 1 hour with 15 times the theoretical amount of sodium carbonate (2 molar). Wolessensky (31) has shown that this con-

TABLE IX. EFFECT OF PRESENCE OF DIFFERENT NITRATES  
(0.01 molar K<sub>2</sub>SO<sub>4</sub>, hot precipitation in 5 minutes by 0.05 molar BaCl<sub>2</sub>, 5 per cent in excess)

HCl Molarity	NO <sub>3</sub>	KNO <sub>3</sub>	NaNO <sub>3</sub>	NH <sub>4</sub> NO <sub>3</sub>	LiNO <sub>3</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	HNO <sub>3</sub>
		Gram	Gram	Gram	Gram	Gram	Gram
Digested 24 Hours Cold							
None	0.01	0.8202	0.8180	0.8195	0.8192	0.8194	..
None	0.1	0.8204	0.8190	0.8219	0.8301	0.8304	..
Digested 12 Hours Hot							
0.01	0.01	0.8153	0.8144	0.8148	0.8163	0.8151	0.8154 <sup>a</sup>
0.01	0.1	0.8211	0.8191	0.8188	0.8290	0.8178	0.8196 <sup>a</sup>

<sup>a</sup> No HCl added.

verts more than 99.5 per cent of the barium sulfate to barium carbonate.

The filtrate and washings from this decomposition were neutralized with hydrochloric acid, additional potassium chloride was added, and the solution was made up to standard volume. Aliquot portions were mixed with sulfuric acid and sodium diphenylamine sulfonate, and the color was matched in a colorimeter with standards containing known amounts of potassium nitrate as recommended by Kolthoff and Nojonen (16). The nitrate determined in this way and the potassium removed by one reprecipitation are given in connection with the ignition losses in Table VII.

Qualitative tests were applied to both the first and the latter portions of material removed from contaminated barium sulfate precipitates by the above methods of decomposition. These gave direct confirmation to the belief that contaminating ions are not merely adsorbed on the crystal surface but are distributed throughout the body of the material.

**COMPARISON OF POTASSIUM SULFATE WITH OTHER SULFATES.** The weights of precipitates obtained from potassium sulfate have been compared under certain conditions with those obtained from sodium sulfate, ammonium sulfate, and free sulfuric acid. The results given in Table VIII show slight differences for the three salts. Since the free sulfuric acid makes the pH of the solution different from that where potassium, sodium, or ammonium salt was used, the results were not strictly comparable. Where hydrochloric acid was added in equal amount to all the solutions, even this difference became small. Since some of the original sulfate is always carried down by precipitated barium sulfate (1), the above differences are to be expected.

**EFFECT OF DIFFERENT NITRATES.** The effect of potassium on the weight of precipitate is compared in Table IX with that of sodium, ammonium, lithium, and magnesium nitrates,



and with nitric acid. The differences are slight for 0.01 molar nitrate. At 0.1 molar the effect of lithium and magnesium nitrates is more than twice that of the potassium, sodium, and ammonium salts.

**PRESENCE OF CHLORIDES.** The effect of alkali chloride has been tested under certain of the conditions that gave best results for precipitation in the presence of nitrate. Comparison of Table X with Figure 1 indicates that in the presence of alkali chloride the weight of precipitate is slightly lower (1). This effect is opposite in direction to that of nitrate, and where the two are present the errors partly compensate each other.

Under the conditions indicated by this investigation for the determination of sulfate in the presence of nitrate, the error due to the presence of alkali chloride is as great or greater than that due to the presence of nitrate.

TABLE X. EFFECT OF PRESENCE OF CHLORIDES

(Barium sulfate precipitated hot in 5 minutes)

HCl Molarity	BaCl <sub>2</sub> to 5 Per Cent in Excess KCl Molarity	BaSO <sub>4</sub> Gram	BaCl <sub>2</sub> to 50 Per Cent in Excess KCl Molarity	BaSO <sub>4</sub> Gram
Digested 12 Hours Hot				
None	0.1	0.8153	...	....
0.001	0.1	0.8121	...	....
0.01	0.01	0.8132		
	0.1	0.8112	0.1	0.8094
	0.1 NaCl	0.8113		
	0.1 NH <sub>4</sub> Cl	0.8132		
0.001 (+ KNO <sub>3</sub> )	..	....	0.1 KNO <sub>3</sub>	0.8176
0.01 (+ KNO <sub>3</sub> )	0.1 KNO <sub>3</sub>	0.8135	0.1 KNO <sub>3</sub>	0.8163
Digested 24 Hours Cold				
0.01 (+ KNO <sub>3</sub> )	..	....	0.1 KNO <sub>3</sub>	0.8111

### General Discussion

The results in Table VIII indicate that potassium sulfate gives lower results than free sulfuric acid or the sodium and ammonium salts, as Karaoglanow (15) has stated. All the nitrates studied except nitric acid (Table IX) cause high results (8, 15). Lithium (9) is especially bad in this respect and magnesium equally so under certain conditions. Usually the effect of potassium nitrate is slightly greater than that of sodium and ammonium nitrates (5, 15).

These differences and the errors themselves are small for solutions 0.01 molar with respect to nitrate where the precipitate is formed slowly from hot solution in the presence of 0.01 molar hydrochloric acid and digested for 12 hours.

The presence of hydrochloric acid in concentrations between 0.01 and 0.001 molar holds down the effect of concentrations of potassium nitrate up to 0.01 molar, but unless the solution is digested hot, the precipitation is incomplete in this range and this effect increases greatly for potassium nitrate concentrations above 0.01 molar. This may be explained by assuming the presence of a complex ion or compound in the nitrate solution which holds back a part of the sulfate.

The tables and figures indicate that there is a considerable tolerance of nitrates in quantitative barium sulfate precipitation within a certain range of conditions.

### Recommended Procedure

For sulfate solutions 0.01 molar or less the solution is made acid between 0.01 and 0.001 molar with hydrochloric acid (1, 10). Barium chloride solution 0.05 molar is added slowly dropwise (about 5 minutes for equivalent amounts) to the hot solution with constant stirring until about 50 per cent excess is

present. The precipitate and solution are kept at about 80° to 90° C. on a hot plate for 12 hours, then filtered through a filtering crucible, washed by decantation and on the filter with 200 to 300 cc. of water, and dried to constant weight at 110° to 120° C. Under these conditions the weight of precipitate is low by 2 to 3 parts per 1000 in the absence of nitrates, 1 to 2 parts per 1000 low in the presence of 0.01 molar nitrate in the original solution, and 1 to 2 parts per 1000 high in the presence of 0.1 molar nitrate in the original solution, and 1 to 2 parts per 1000 high in the presence of 0.1 molar nitrate in the original solution if lithium is absent. The presence of alkali chlorides lowers the weight of precipitate, counteracting the effect of nitrate (15).

### Summary

A study has been made of the influence of various factors upon the weight of barium sulfate precipitated from solution both in the presence and in the absence of potassium nitrate.

Evidence indicates the possible existence of a complex ion or complex-compound form of sulfate in potassium nitrate solutions which retards precipitation under certain conditions.

Barium sulfate precipitated from molar potassium nitrate solution carries down potassium nitrate within the precipitate at the time of precipitation. The precipitation is incomplete however, and if the solution is allowed to stand at room temperature precipitation continues slowly for days with continued contamination of the precipitate. If the solution is kept hot (80° to 90° C.), the slow precipitation observed at a lower temperature does not occur.

If potassium nitrate is not added until after precipitation the precipitate of barium sulfate is not contaminated.

Barium sulfate precipitates formed in the presence of nitrate are more sensitive to influence by variations in conditions of precipitation and treatment than are the precipitates formed in the absence of nitrate.

Information as to the nature and extent of the contamination of barium sulfate precipitates formed in the presence of nitrates indicates that the contamination is distributed throughout the precipitated material.

Under most conditions the presence of potassium nitrate produces high results. This overweight may be as much as 230 parts per 1000 above the value required by theory.

Conditions have been defined within which barium sulfate may be determined quantitatively to a precision of 2 parts per 1000 in the presence of nitrate in amounts equivalent to that of the sulfate present.

The effect of ignition upon precipitates contaminated with potassium nitrate has been studied and losses in weight have been found to increase with increased contamination. The extent of contamination of precipitates has been studied while the contaminants are in their original, unignited form.

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# Determination of Copper in Paris Green and Ores

## A Ceriometric Method

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THE development of many analytical methods wherein ceric sulfate is used as the standard oxidant has been reported in recent years (5, 6, 7). The progress shown in the last ten years has been due to the production of a better grade of ceric salts, an increased interest in the reagents of higher oxidizing potentials, and the development of suitable indicators for these reagents. Diphenylamine, the first indicator used for ceric sulfate, has largely been replaced by more stable and more sensitive compounds having higher oxidizing potentials, such as *o*-phenanthroline ferrous complex and sodium diphenylamine sulfonate (2, 6, 10). In comparison to the more commonly used oxidants, potassium dichromate and permanganate, ceric sulfate has many distinct advantages (6, 9, 11).

Recently Stegeman and Englis (9) reported a method for determining reducing sugars in which a standard solution of ceric sulfate is used to oxidize the cuprous oxide formed by the action of those sugars on Fehling's solution. It should therefore be possible to make use of this reaction between cuprous oxide and ceric sulfate for the determination of copper in Paris green and ores. The present work is a study of the application of ceric sulfate as a standard oxidant to such a procedure, which also involves the preliminary separation of cuprous oxide free from interfering substances. In the case of Paris green there is sufficient arsenite present to reduce all the copper to cuprous oxide which is insoluble in alkaline solution, but in the case of copper ores not only must interfering substances, such as iron and lead, be removed, but arsenite must also be added to reduce the copper. In either case the cuprous oxide can be filtered, washed free from excess arsenite, and quantitatively oxidized with standard ceric sulfate solution, using either *o*-phenanthroline ferrous complex or sodium diphenylamine sulfonate as indicator.

### Preparation of Solutions

**Sodium Hydroxide.** A 2 per cent solution.  
**Sodium Arsenite.** Fifteen grams of arsenic trioxide were dissolved in 20 ml. of 6 *M* sodium hydroxide solution, the solution was filtered if not clear, and diluted to 100 ml.

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***o*-Phenanthroline Ferrous Complex.** A 0.025 *M* solution obtainable in the regular trade channels (12).

**Sodium Diphenylamine Sulfonate.** A 0.01 *M* solution prepared in the usual manner from the barium salt (10).

**Ceric Ammonium Sulfate.** A 0.1 *N* solution made as described by Willard and Furman (12) and standardized against a standard iron ore. A solution of ceric ammonium nitrate may be used as indicated by Smith, Sullivan, and Frank (8).

**Ferrous Ammonium Sulfate.** A 0.1 *N* solution prepared in the usual manner and standardized against the ceric ammonium sulfate solution at the time of use.

### Procedure for Paris Green

An accurately weighed sample of 0.3 to 0.4 gram was transferred to a 400-ml. beaker to which were added 100 ml. of 2 per cent sodium hydroxide solution. The mixture was heated to boiling and stirred until all the green compound was converted into the red cuprous oxide. Normally Paris green contains more than enough arsenite to reduce all the copper to cuprous oxide. If the precipitate should contain any black particles, it should be dissolved in dilute sulfuric acid, 2 to 5 ml. of sodium arsenite solution should be added followed by 6 *N* sodium hydroxide solution until a green precipitate forms, and the mixture should then be heated and digested until only a red or yellowish-red precipitate remains.

After digestion on the hot plate until the supernatant liquid was clear, the solution was filtered cold on a Gooch crucible and the residue on the filter was washed with cold distilled water until the volume of the filtrate was about 250 ml. Since cuprous oxide is slowly oxidized by atmospheric oxygen the filter was not sucked completely dry during the filtration. The crucible containing the residue was placed in the original beaker, an excess of 0.1 *N* solution of ceric ammonium sulfate was added, and the mixture was stirred thoroughly. Excess was indicated by the yellow color imparted to the solution. Special care was taken to disintegrate the asbestos mat thoroughly, heating carefully to boiling and stirring until all the cuprous oxide had dissolved.

To the cold solution 100 ml. of recently boiled and cooled distilled water were added, followed by an excess of accurately weighed ferrous ammonium sulfate or 15 to 20 ml. of a 0.1 *N* solution of the salt. In the presence of excess ferrous ions the yellow color of the solution changed to the pale blue of cupric ions. With either 2 drops of *o*-phenanthroline ferrous complex or 8 drops of sodium diphenylamine sulfonate solution as indicator the excess ferrous ammonium sulfate was titrated with more of the 0.1 *N* solution of ceric ammonium sulfate and the total volume was noted. The volume of ceric ammonium sulfate solution equivalent to the ferrous ammonium sulfate added was calculated, subtracted from the total volume used, and from



TABLE I. DETERMINATION OF COPPER IN PARIS GREEN

Sample Number	Cupric A. O. A. C. iodide method %	Oxide Found Ceric sulfate method %	Deviation %	Indicator
19	24.99	25.03	+0.04	Diphenylamine
20	25.09	25.05	-0.04	Diphenylamine
21	26.42	26.46	+0.04	<i>o</i> -Phenanthroline
22	27.38	27.35	-0.03	Diphenylamine
23	30.45	30.50	+0.05	Diphenylamine
24	30.91	30.92	+0.01	Diphenylamine
25	29.81	29.78	-0.03	<i>o</i> -Phenanthroline
26	29.98	29.94	-0.04	Diphenylamine
27	29.93	29.89	-0.04	<i>o</i> -Phenanthroline
28	49.41	49.40	-0.01	<i>o</i> -Phenanthroline
29	29.79	29.80	+0.01	<i>o</i> -Phenanthroline
30	30.13	30.12	-0.01	<i>o</i> -Phenanthroline

TABLE II. DETERMINATION OF COPPER IN ORES

(Indicator, *o*-phenanthroline ferrous complex)

Sample Number	Copper Found Iodide method %	Ceric sulfate method %	Deviation %
1	3.03	3.04	+0.01
2	3.94	3.89	-0.05
3	5.37	5.32	-0.05
4	6.27	6.22	-0.05
5	7.27	7.29	+0.02
6	15.02	15.02	0.00
7	14.36	14.39	+0.03
8	13.23	13.22	-0.01
9	22.31	22.35	+0.04

the remaining volume the percentage of copper as cupric oxide was calculated.

### Procedure for Copper Ores

An accurately weighed sample of 0.25 to 1 gram, depending upon the copper content, was transferred to a casserole and warmed on the hot plate with a mixture of 10 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid for at least half an hour. With sulfide ores any small globule of melted sulfur which formed a dark lump on solidification was removed and washed and then ignited in a crucible. The dark residue was dissolved in nitric acid and the solution was rinsed into the main solution.

After the addition of 5 ml. of concentrated sulfuric acid the mixture was carefully heated until dense white fumes of sulfur trioxide were evolved. The copper sulfate in the residue was dissolved by warming with 25 ml. of water. To the cooled solution an excess of 15 *N* ammonium hydroxide was added with thorough stirring to precipitate the iron as ferric hydroxide and to convert the copper into the deep blue soluble complex.

The mixture was filtered into a 400-ml. beaker and the residue on the paper was washed with 3 *N* ammonium hydroxide until the washings came through colorless. By means of a stream of water from the wash bottle the residue was rinsed back into the casserole and just enough concentrated sulfuric acid was added to dissolve the iron precipitate. Ferric hydroxide was then reprecipitated by slowly adding 15 *N* ammonium hydroxide until the solution was basic after thorough stirring. With bits of filter paper added to hasten filtration, the solution was filtered through the original paper and the residue was washed with 3 *N* ammonium hydroxide until the volume of the combined filtrates was about 250 ml. This method of double precipitation of the iron, which is also used in the colorimetric determination of copper with ammonia (3), is more accurate, more conveniently carried out, and much more rapid than the process of precipitating the copper by aluminum strips as originally done in the iodide method for copper. According to Heath (3), results with samples containing from 25 to 35 per cent of iron and aluminum oxides showed never more than 0.04 per cent of copper in the residue on the filter after the second precipitation and sometimes no copper at all.

After the addition of glass beads to the filtrate to lessen the danger of bumping, it was carefully evaporated to about 100 ml. to remove excess ammonia. The solution was then boiled with 10 ml. of 6 *N* sodium hydroxide solution until black cupric oxide precipitated and the supernatant liquid was colorless, using more sodium hydroxide if necessary. The black precipitate was dissolved in dilute sulfuric acid, 2 ml. of sodium arsenite solution were added, the solution was diluted to about 100 ml., and 6 *N* sodium hydroxide solution was added as long

as any yellowish green precipitate was formed. This mixture was heated to boiling and stirred to convert the precipitate into the red cuprous oxide. From this point the same procedure was followed as for Paris green above. This precipitate is likely to be more flocculent and more yellowish red than that from Paris green. To ensure successful filtration it should be digested a longer time than in the case of Paris green, and for thorough washing a much larger amount of water should be used.

### Results

The results of the determination of copper in twelve samples of Paris green and nine ores are shown, respectively, in Tables I and II, which also include for comparison the figures obtained by the iodide method (1, 4). Each result is the average of duplicate determinations.

### Discussion

Commercial Paris greens were used with the exception of No. 28, which was a sample of cupric arsenite requiring the addition of sodium arsenite to cause complete reduction of the copper to cuprous oxide.

The ceric sulfate method is capable of giving results for copper in Paris green and ores which are within  $\pm 0.05$  per cent of those obtained by the iodide method. Results may be duplicated on the same sample with a precision of  $\pm 0.10$  per cent.

### Summary

A method has been developed for the use of ceric sulfate as the standard oxidant in the determination of copper in Paris green and in ores and the results have been favorably compared with those obtained by the iodide method.

The advantages of the cerimetric method over the iodide method are: It is more rapid and much less tedious, as fewer steps are involved; in the titration the end point is much more easily detected because of the distinct change in color of the solutions of the indicators, *o*-phenanthroline ferrous complex and sodium diphenylamine sulfonate, are stable for many months in contrast to the unstable starch solution; and although ceric sulfate is generally regarded as being somewhat expensive, the cost of the amount used in a determination is less than that of the potassium iodide required in a determination by the iodide method.

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# Determination of Strontium in the Presence of Calcium

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FOR some years a study has been under way in these laboratories involving the preparation of various alkaline earth salts with the help of organic solvents (2, 4, 7, 9, 10, 11, 14). For this work, accurate analysis of strontium salts in the presence of calcium compounds was necessary.

Many methods have been suggested for the separation of strontium from calcium, which is made difficult by the small differences in the solubilities of the salts of the two metals. To increase the solubility the use of certain solvents other than water has been recommended. Browning (3) found that calcium nitrate is completely soluble in amyl alcohol while strontium nitrate is practically insoluble. Fresenius (6) separated the nitrates of barium and strontium from calcium by using a mixture of ether and ethyl alcohol. Rawson (8) separated calcium nitrate from strontium and barium nitrates by means of concentrated nitric acid, in which calcium nitrate is soluble. Treadwell and Hall (12) offer a procedure for the analysis of alkaline earth metals in which calcium nitrate is dissolved by absolute alcohol while the nitrates of strontium and barium remain undissolved.

TABLE I. SOLUBILITIES OF NITRATES OF CALCIUM AND STRONTIUM

(Per cent of salt in solution at 25° C.)		
Solvent	Sr(NO <sub>3</sub> ) <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>
Ethyl alcohol	0.02	52.0
Propyl alcohol	0.02	36.5
Isobutyl alcohol	0.01	25.0
Amyl alcohol	0.003	13.3
Acetone	0.02	58.5

Ans and Siegler (1) present a comparison of the solubilities of the nitrates of strontium and calcium in different solvents. From their data, which were obtained from studies by Eidman (5) and are only semiquantitative in character, ethyl, propyl, isobutyl, and amyl alcohols and acetone may be selected as suitable solvents to use in the separation of calcium nitrate from strontium nitrate. The quantitative effects of these solvents are shown in Table I, taken from an article by Williams and Briscoe (13).

TABLE II. SEPARATION OF STRONTIUM NITRATE FROM CALCIUM NITRATE BY ACETONE

Strontium Nitrate Taken Grams	Calcium Nitrate Added Grams	Strontium Nitrate Recovered Grams	Recovery %
1.5000	0.10	1.4981	99.88
2.0000	2.00	1.9977	99.89
1.0010	0.50	1.0008	99.98
1.5001	0.50	1.4996	99.97
2.0006	0.50	1.9999	99.97

Because of the usual difficulty in making this separation, an outline of the procedure which the authors have used may be of interest. This is based on the observation of Williams and Briscoe (13), that at 25° C. strontium nitrate is only 0.02 per cent soluble in acetone while calcium nitrate dissolves in acetone to the extent of 58.5 per cent.

Since acetone appeared to be favored for the separation of calcium nitrate from strontium nitrate, quantitative data were obtained. Weighed amounts of strontium nitrate and calcium

nitrate were dissolved in water, 2 ml. of concentrated nitric acid were added, the solution was evaporated to dryness on a steam hot plate, the mass was allowed to cool, and 25 ml. of acetone were added. The acetone was allowed to remain in contact with the solid for one hour with occasional shaking. The undissolved portion was transferred to a weighed Gooch crucible, washed with acetone, and weighed as Sr(NO<sub>3</sub>)<sub>2</sub>. The results are shown in Table II.

The following method, which proved convenient and accurate, was evolved from the above:

A synthetic mixture of strontium chloride with calcium chloride and calcium sulfate was extracted with methanol, filtered, and made up to exactly 250 ml. with distilled water. The extract contained strontium chloride and calcium chloride, since calcium sulfate is insoluble. Calcium sulfate was added to the synthetic mixture because in the analysis for which this method was desired calcium sulfate was present. Fifty milliliters of the extract were pipeted into a 250-ml. beaker and warmed to 50° C. on a steam hot plate, and 10 ml. of freshly prepared ammonium carbonate solution were added slowly. This converted the strontium chloride and calcium chloride into the corresponding insoluble carbonates which were left on a hot plate for 10 minutes, then allowed to cool.

The mixed carbonates were filtered into a Gooch crucible, then dissolved in dilute nitric acid. This gave an aqueous solution of the mixed nitrates which was evaporated to dryness on a steam hot plate. After cooling, 25 ml. of anhydrous acetone were added and left in contact with the mixed nitrates for one hour with occasional agitation. The acetone dissolved all the calcium nitrate and left the strontium nitrate, quantitatively. The strontium nitrate was transferred to a weighed Gooch crucible, washed with more acetone, dried in an oven, and weighed.

TABLE III. SEPARATION OF STRONTIUM CHLORIDE FROM CALCIUM CHLORIDE

(Using the procedure outlined above. The following are blanks.)			
Strontium Chloride Centimoles	Calcium Chloride Centimoles	Calcium Sulfate Centimoles	Strontium Recovery %
1.000	0.500	1.000	99.7
1.000	0.500	1.000	99.9
1.000	0.500	1.000	99.7
1.000	1.000	1.000	99.9
1.000	1.000	1.000	99.8

Blanks run on synthetic mixtures according to the above procedure gave results varying from 99.7 to 99.9 per cent recovery, as detailed in Table III.

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# Electrometric Indicators with the Dead-Stop End-Point System

## Applications to Neutralization and Precipitation Reactions

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IT HAS been suggested by Foulk and Bawden (2) that the dead-stop electrometric indicator system is applicable to neutralization reactions as well as to oxidation-reduction reactions, and a slightly modified system of polarized platinum-platinum electrodes has been described by Wright and Gibson (4).

In the present work the suggestion of Foulk and Bawden with regard to neutralization reactions has been extended to include precipitation reactions. A procedure is described for the use of substances to obtain an electrometric end point in titrations by the dead-stop end-point system in those cases in which an end point is otherwise not given. The name "electrometric indicator" is proposed for such substances, as their role in electrometric titrations is analogous to that of color indicators in volumetric analysis. Willard and Fenwick (3), the first to give an example of such an indicator, found that the addition of hydrogen peroxide to acid or alkaline solutions gave a sharp, but not permanent, end point in neutralization titrations by their bimetallic electrode system. For a discussion of the apparatus and the essential features of the procedure the work of Foulk and Bawden (2) should be consulted.

### Neutralization Reactions

Iodate and iodide as electrometric indicators.<sup>1</sup> If both iodate and iodide are added to a solution of a base, no reaction takes place but the anode of a polarized electrode system will be depolarized by the reducing action of the iodide. If, now, the base is titrated with acid, a reaction between the iodate and iodide occurs as soon as the pH value becomes slightly less than 7. The trace of iodine liberated depolarizes the cathode. Both electrodes being depolarized, current flows, giving the end point which is registered by the permanent deflection of the galvanometer pointer.

TABLE I. WEIGHT TITRATIONS

(Approximately 0.50 *N* sodium hydroxide with 0.25 *N* hydrochloric acid)

Weight of Alkali	Weight of Acid	Ratio of Alkali
Grams	Grams	to Acid
23.5191	46.8729	20:39.94
20.6122	41.1440	20:39.92
19.9538	39.8288	20:39.92
20.5849	41.0705	20:39.90
19.6670	39.2446	20:39.90

To demonstrate the use of potassium iodide and iodate as electrometric indicators, titrations were made of 25-ml. portions of 0.5 *N* sodium hydroxide with 0.25 *N* hydrochloric acid. An impressed potential of a fraction of a volt was used to balance the e. m. f. of polarization; 10 drops each of 0.1 molar potassium iodate and iodide were added to the alkaline solution.

The resistance was then adjusted so that the pointer of the galvanometer took a position at or near zero. When the volume of the solution added from the buret was within a milliliter or so of the equivalence point, momentary deflections of the galvanometer needle, increasing in intensity, gave warning of the approaching end point, and when the end of the titration was reached the pointer took up a permanent position away from zero. A series of titrations was made by using weighing burets, and completing the titration with 0.0125 *N* hydrochloric acid added from a volume buret, this volume being converted to weight of 0.25 *N* hydrochloric acid. The results are shown in Table I.

<sup>1</sup> The first experimental work with a mixture of iodide and iodate as an electrometric indicator was done at Professor Foulk's suggestion by Henry F. Palmer, a graduate student in the Department of Chemical Engineering in The Ohio State University.

Potentials ranging from 1 to 10 millivolts were impressed during a titration, other conditions being kept constant. Largest deflections at the end point were obtained by employing as large an impressed voltage as possible, and still maintaining a state of balance with the back e. m. f. of polarization.

Simple colorimetric measurements of the amount of iodine set free with various ratios of iodide and iodate were made, using 0.1 molar solutions of potassium iodide and iodate and the same concentrations of acid. It was found, as was expected, that an excess of iodate over the reaction quantity set free a larger amount of iodine. The molecular reaction quantities measured into a color-comparison tube formed the standard by which the colorimetric measurements were made. The intensities of color produced by varying the concentrations of iodide-iodate were then measured. Equal molar concentrations of iodide and iodate liberated the largest amount of iodine with the same pH value.

TABLE II. WEIGHT BURET TITRATIONS

(Approximately 0.5 *N* hydrochloric acid with 0.5 *N* sodium hydroxide)

Weight of HCl Solution	Weight of NaOH Solution	Ratio of HCl to NaOH	Deviation from Average, 10:10.397
Grams	Grams		
12.8684	13.3755	10:10.394	-0.003
21.9421	22.7686	10:10.377	-0.020
5.7419	5.9812	10:10.415	+0.018
10.9194	11.3594	10:10.403	+0.006

Keeping the molecular ratio of iodide-iodate the same titrations were then made in which the concentration of the iodide-iodate mixture in the titrated solutions was varied in order to find the optimum amount of indicator substance in this ratio to be used in a titration. An amount corresponding to 10 drops each of the 0.1 molar solutions was found to be the most suitable and was therefore used in all titrations.

The pH value necessary to produce the end point was observed to be near the neutral point. That the acidity required to give the dead-stop end point is very slight was proved by results obtained from potentiometric measurements of the pH value of solutions of completed titrations. The average pH value of the solutions was found to be 6.67.

Iodine as electrometric indicator. The iodide-iodate mixture described above will not work in acid solution because the two substances react; therefore another indicator was sought. Iodine was found to serve the purpose. When added to an acid solution, it keeps the cathode depolarized but has no effect on the anode. On titration, the first excess of alkali reacts with the iodine to form a trace of iodide which then depolarizes the anode. This permits a flow of current which registers on the galvanometer, thus giving the end point. A 3 per cent alcoholic solution of iodine in alcohol was used for the indicator substance in the titrations of acids with bases. Experiments showed that 2 drops produced maximum decrease in the polarization potential of the cathode. This amount of the iodine indicator was then used in the subsequent titration.

A series of titrations was made with approximately 0.5 *N* hydrochloric acid and sodium hydroxide using volume burets and finally, to prove the precision of the method, with weighing burets. Table II gives these latter results. The



end point coincides with the color changes of dibromothymolsulfonphthalein.

The titration of a strong acid with a weak base, such as hydrochloric acid with ammonium hydroxide, gave a reproducible end point. Two drops of iodine indicator were used. The end point was sensitive and coincided closely with the color change of phenol red.

**HYDROGEN PEROXIDE AS ELECTROMETRIC INDICATOR.** Experiments showed that hydrogen peroxide is an admirable indicator for titrations with both acids and bases, its action depending on the sharp difference in its reduction potential in acid as compared with that in alkaline solutions. In alkaline solutions the degree of polarization of the anode is low and that of the cathode high. As the equivalence point is approached in the titration of bases with acids, this difference in degree of polarization of the two electrodes increases, and at the equivalence point the increase is sharp; the anode becomes completely polarized and the depolarization of the cathode is increased. These two effects are additive, which makes the end point as registered by the galvanometer all the sharper. On titrating an acid with a base, the above conditions are reversed. Hydrogen peroxide, therefore, is a reversible electrometric indicator for the dead-stop end-point system, in which it differs from the iodate-iodide mixture and the iodine.

TABLE III. WEIGHT BURET TITRATIONS			
(Approximately 0.5 N hydrochloric acid with 0.5 N sodium hydroxide)			
Weight of HCl Solution Grams	Weight of NaOH Solution Grams	Ratio of HCl to NaOH	Deviation from Average, 10:10.393 <sup>a</sup>
10.5835	10.9800	10:10.375	-0.018
12.4222	12.9415	10:10.418	+0.025
10.9563	11.3750	10:10.382	-0.011
16.8931	17.5637	10:10.397	+0.004

<sup>a</sup> Average ratio of HCl to NaOH using I<sub>2</sub> as the indicator, 10:10.397 (see Table II).

Hydrogen peroxide is unique in its action as an indicator substance because it may be used in either acid or alkaline solutions. The same experimental conditions governing titrations with the iodide-iodate indicator were found to apply to the titrations with peroxide. The indicator used was the ordinary 3 per cent commercial solution which had been neutralized with sodium hydroxide. By experimentation it was found that 4 drops of this solution was the optimum amount to use in the titrations of acid with base. Table III gives results by this method.

Precipitation Reactions

**NITRITE AS ELECTROMETRIC INDICATOR.** The scheme of electrometric analysis as described for neutralization reactions may with appropriate indicators be applied to titrations of the halides and cyanides with silver nitrate. The apparatus is identical with that for neutralization titrations. The general conditions that obtain when one attempts to titrate the halides with silver by the dead-stop end-point system are the same as those in neutralization reactions—that is, no end point is given. In a search for an indicator it was found that sodium nitrite served to keep the anode depolarized during the titrations; therefore, it was used as the indicator in all cases save those of iodides and cyanides which are themselves anodic depolarizers. Silver ions serve to depolarize the cathode at the equivalence point, and a sharp reproducible end point is obtained. That the action of silver ions at the cathode is responsible for the end point was proved by segregating the electrodes by means of a salt bridge and then studying the action of silver nitrate, sulfate, and acetate on the cathode and anode separately. In no case did the addition of a silver salt affect

the anode, while each of the above-named salts produced a reduction of potential at the cathode. As an explanation of the phenomena at the cathode, it is assumed that the cathode during the titration has atomic hydrogen adsorbed on its surface, not as a static layer but in equilibrium with hydrogen ions in the solution. At the equivalence point there is a sudden increase in the concentration of silver ions, which tend to discharge on the cathode at a lower potential. A new system of lower equilibrium potential is thereby established—namely, that between silver and silver ions. The cathode acquires the electromotive characteristics of a silver electrode, although there is no visible deposit of that metal.

TABLE IV. WEIGHT TITRATION		
(Approximately 0.1 N potassium iodide with 0.1 N silver nitrate)		
Weight of AgNO <sub>3</sub> Solution Grams	Weight of KI Solution Grams	Ratio of Weights of Solutions, AgNO <sub>3</sub> :KI
22.1525	21.5623	1.0278
15.9615	15.5150	1.0288
11.9770	11.6460	1.0284
11.3260	10.9970	1.0290
19.2619	18.7355	1.0281
		Av. 1.0285

To prove that the end point coincides with the equivalence point, two portions of the filtrates from several completed titrations were tested by adding 0.1 N silver nitrate solution to the one portion and the same volume of 0.1 N sodium chloride solution to the other. The turbidities were then compared. The tubes containing the excess chloride showed only a slightly greater turbidity than those with the excess of silver, proving that only a very small excess of precipitant is necessary to give the end point. The optimum amount of nitrite indicator substance to be added was established by measuring the cell potentials after the addition of a 0.1 N sodium nitrite solution to be titrated. The amount which was most effective in depolarization of the anode was found to be 2 drops of 0.1 N solution. A test was made to find the minimum concentration of silver ions that would produce a sharp end point. Twenty-five milliliters of 0.1 N sodium nitrate solution were diluted to 100 ml. in the titration vessel, this being the quantity of electrolyte present at the end of a typical titration. The addition of one drop of 0.001 N silver nitrate to this sodium nitrate solution gave a sharp end point. Typical titrations were run with the same volume of reagents but varying the alkalinity by adding different volumes of 0.1 N sodium hydroxide solution, keeping the pH value below 8.5, above which value silver oxide is supposedly formed. Making the solution slightly alkaline gives a more sensitive end point, decreasing the degree of reversibility of the electrode reaction. Effects of varying pH values on the acid side were observed by adding increasing volumes of 0.1 N nitric acid and finally more concentrated reagent. As the acidity of the solution was increased, the end point became more sluggish but was still reproducible. The reproducibility of the end point is very high, owing to the large galvanometer deflections produced at the equivalence point. There is no difference in the degree of reversibility of the electrode reaction before and after the end point. That the end point is reproducible with a high degree of precision is indicated in Table IV. **Mixed Halide and Cyanide Determinations** Following a suggestion from the method of Behrend (1), a successful attempt was made to titrate mixtures of chloride and iodide, and of bromide and iodide. Addition of sufficient ammonium hydroxide kept the chloride or bromide in solution



in the form of the ammonia complex until the first drop in potential indicated the complete precipitation of iodide. The solution was then neutralized with nitric acid and the titration continued until the second drop in potential occurred, corresponding to the complete precipitation of chloride or bromide. Excellent results were obtained.

In following up the possible uses of silver nitrate with the dead-stop end point, potassium cyanide was titrated with interesting results. This salt was found by experiment to be an anodic depolarizer like potassium iodide and sodium nitrite, which makes it unnecessary to add an indicator. In titrating potassium cyanide, two galvanometer deflections are produced which correspond quantitatively to the complete formation of  $KAg(CN)_2$  and  $Ag_2(CN)_2$ , respectively. When 0.1 *N* silver nitrate is used as the titrating agent, the galvanometer deflection produced at the potassium argenticyanide equivalence point is only a flash, the light spot returning immediately to zero, but the deflection is very pronounced, going the full galvanometer scale, so that results are very readily reproduced. The second deflection corresponds to the complete precipitation of silver cyanide. A tentative explanation of the two end points produced is based on the assumption that the lag between complete formation of the silver cyanide complex and the beginning of precipitation of the silver cyanide is sufficient to furnish a concentration of silver ions which will momentarily depolarize the cathode.

Experiments in which 25 ml. of approximately 0.1 *N* potassium cyanide were titrated with 12.9 ml. of 0.1 *N* silver nitrate at the potassium argenticyanide equivalence point

gave 25.75, 25.85, 25.80, 25.65, 25.80, and 25.80 ml. of total silver nitrate.

### Summary

This paper describes a simple and accurate method for the electrometric titration of acids, bases, halides, cyanides, and silver ions. Results are as highly reproducible as those obtained by the present accepted methods of electrometric analysis. The method has the advantage of using two simple platinum wire electrodes, and it eliminates the use of a reference electrode. The electrodes are seldom, if ever, poisoned, which removes the difficulty in the use of certain other electrode systems. Adequate warning of the approach of the end point is given by momentary deflections of the galvanometer pointer. Since the end point is reversible, back-titration is possible.

Titration of copper, mercury, and other metallic ions should be possible by the same principle employed in the titrations of silver ions. This opens a new field for the volumetric determination of the metallic ions with a low deposition potential.

The titration of zinc with ferrocyanide should be investigated, because the ferrocyanide would serve as an anodic depolarizer.

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# Preparation of Carbon Electrodes for Spectrographic Analysis

## Two Useful Lathe Tools

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THE exposure time for complete volatilization of a sample of plant ash in spectrographic analysis is dependent, among other factors, on the depth of the cavity drilled in one end of an electrode to receive the sample, and on the thickness of the crater wall. The diameter of the carbon rods used in this study is 8 mm. (0.3125 inch). A cavity size which has proved suitable in this work has the following dimensions: inside diameter, 6 mm. (0.25 inch); depth, 3.5 mm. This crater will hold 10 to 25 mg. of dried plant material or 0.1 ml. of liquid. A wall thickness of 0.3 mm. is a good compromise. Using electrodes of the above dimensions (with a 15-ampere and 150-volt current) pointed upper electrodes (8-mm. rods pointed in a pencil sharpener) and an arc length of 3.0 mm., the ash in a 10-mg. sample of dried plant tissue is volatilized completely in 60 seconds.

If the wall is too thin, liquid will leak through, and salt will be deposited on the outside of the wall when the solution is evaporated to dryness; if the wall is too thick, the arc will wander and too much time is required to burn the wall down to the cavity floor, which is essential if the last trace of fused ash is to be burned off. Too thick a wall also unduly increases background on the plate. Since in the course of analytical routine, a large number of electrodes are prepared, it is desirable that facing the end of the electrode, drilling the hole,

and cutting down the outside wall be accomplished in one operation.

A tool was made that answers the above specifications. It was designed to produce craters of uniform wall thickness but variable depths by an adjustment of the set screw as is shown in Figure 1.

By machining the outside of the cavity wall, uniformity of thickness is ensured, so that irregularities in graphite electrodes as purchased become unimportant; a long outside cut of 9.5 mm. when the cavity depth is only 3.5 mm. has the advantage of the smaller diameter 6-mm. (0.25-inch) electrode. It will be noted from Figure 1 that the angle on the cutting edge of the bit has been reduced, so that the depression in the floor of the cavity is comparatively slight. This ensures rapid cleanup of traces of the ash residue when the wall has burned down to the floor.

In spectrographic determination of mercury in plant tissue the authors found that a more intense mercury line is produced at 2536.7 Å. by using an unusually deep electrode cavity (about 15 mm.). With the use of 8-mm. electrodes pointing the wall at the top serves to prevent arc wandering during the short exposure needed to volatilize the mercury present. A tool designed to perform the operations of drilling and pointing, simultaneously, is shown in Figure 2.



consists of a standard 6-mm. twist drill and a steel collar with a set screw on which projects a cutting edge at a suitable angle (about 20°). The depth of the cavity here again can be varied by merely sliding the collar along the drill and tightening the screw.

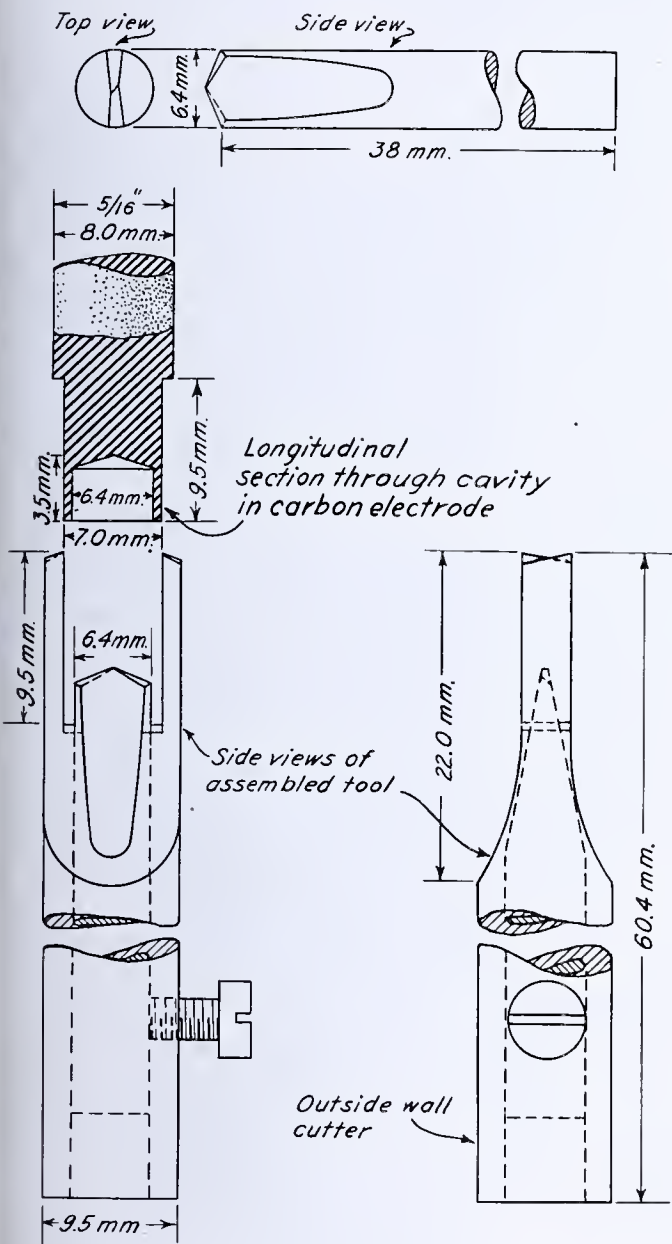


FIGURE 1. CARBON DRILLING AND CUTTING TOOL DRILL BIT

The tools should be made of tool steel and tempered to keep a edge on the cutting parts. Any good tool steel will be satisfactory, but must be protected against corrosion under high humidity conditions by storage in a desiccator or by wrapping in an oiled cloth. Suitable alterations in the given dimensions will permit the use of these designs for producing cavities on electrodes of different diameter than the one the authors are using, and will give different wall thicknesses to suit the requirements of any special material. The electrodes are machined in a small bench lathe in the laboratory. The carbons are allowed to revolve held in a collet on the headstock end, while the tool is fastened in a chuck in the tailstock. This lathe is kept clean and is reserved for the production of electrodes. With a suitable lathe and equipment the procedure can be reversed, with a resultant increase in the number of electrodes produced.

Also, a good drill press combined with an electrode-holding device (chuck, collet, etc.), attached firmly to the bed or base plate, can be substituted where a lathe is not available. For successful production of this thin-walled cavity, both tool and carbon electrode must be held immovable as in a chuck or collet.

Performance has demonstrated that the use of these tools makes possible rapid preparation of electrodes with the desired uniformity of dimensions. Electrodes can easily be produced at the rate of two a minute. The tools should be operated at a minimum speed of 1300 r. p. m.; at slower

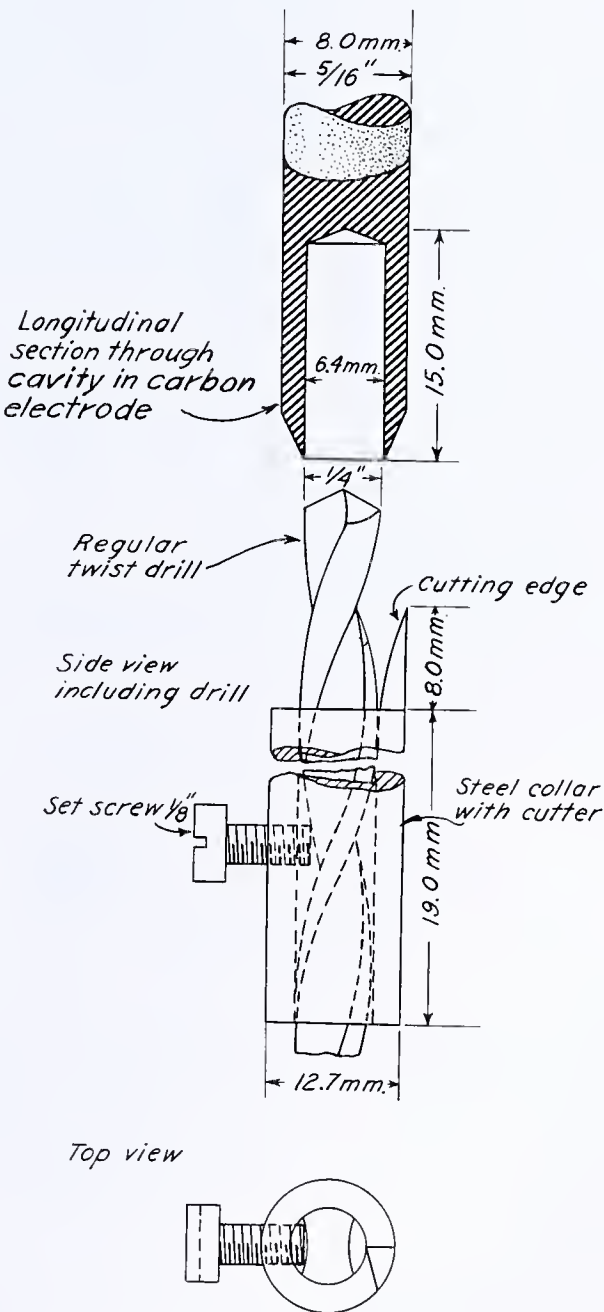


FIGURE 2. CARBON DRILLING AND POINTING TOOL

speeds breakage of the electrode wall is apt to occur. It was pointed out to the authors that this type of tool is less subject to borrowing than the ordinary drills, therefore the contamination danger is avoided.

Acknowledgment

Acknowledgment is hereby made of the help of Leonard Smith of the Bendix Corporation who made the experimental models for this study.



# Sintered-Glass Filters and Bubblers of Pyrex

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SINTERED- or fritted-glass filters and gas distributors have come into general use during recent years (10). Their manufacture is covered by the patents of Schott and Gen., Jena, Germany, who offer an extensive line of fritted-glass filters in the Jena glass (9). Because of the difficulty of sealing the sintered equipment of Jena glass with the borosilicate glass so widely used in this country, workers have made their own sintered Pyrex in various ways. With this situation in mind the authors call attention to the literature on the subject and describe an improvement in the existing methods of preparation, so simple that the average worker can make use of it.

Certain of the more commonly used sintered devices are readily prepared without any special technique or equipment. These include the so-called "filter stick" for filtering liquids as they are removed from containers and gas-distribution tubes for dispersing gases in liquids for aeration, absorption, and washing purposes.

There are two general techniques for the preparation of sintered-glass apparatus. One involves the preparation of a sintered-glass disk which is subsequently fused into the tube; the other sinters and fuses the powdered glass in place in a single operation.

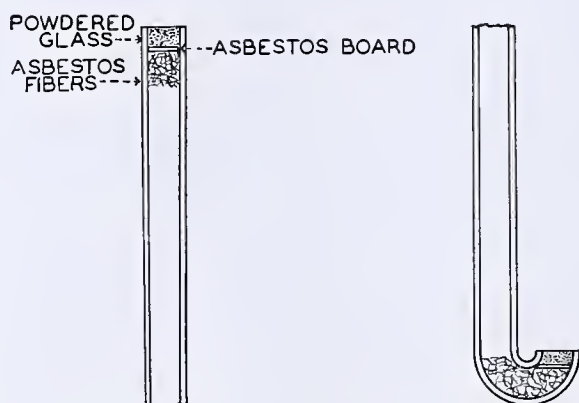


FIGURE 1. FILTER STICK AND GAS DISTRIBUTOR

Several writers (1, 2, 7) have described methods of preparing the disks separately. The principle has also been used by Cool and Graham (3) for the preparation of sintered-glass aeration thimbles. The chief advantage of preparing the disks separately lies in the fact that larger and more uniform disks may be prepared. Its disadvantages are that more elaborate apparatus, greater skill, and a longer time are required.

The second technique, in which the powdered glass is sintered and sealed in place in a single operation, has several modifications. Shatenshtein (11) holds the powdered glass in the tube with carbon rods and sinters in a blast-lamp flame. Kirk (5) places the powdered glass in a small bulb at the end or side of the tube for sintering and then exposes the sintered surface by grinding.

Furnstal and Johnson (4) make use of both techniques and recommend methods involving the use of a temperature-controlled muffle furnace. This is very satisfactory for those who have a large number of sintered-glass devices to prepare, but the equipment and technique are unnecessarily involved for the needs of the average chemist.

The authors have developed a very simple method for preparing sintered-glass plugs in the ends of tubes which satisfy many of the sintered-glass laboratory requirements.

It has been used successfully on tubing up to 10 mm. in outside diameter and on capillary tubes by flaring the ends. The capillary type is described by Kirk (6) for use in quantitative microanalysis.

Scrap Pyrex glass is ground by any convenient method; both the iron mortar and pestle and the power mill are satisfactory. The methods of cleaning and grading recommended by Bruce and Bent (2) are followed. The ground glass is heated with hydrochloric acid, washed with water, dried, and separated into 60 to 80-, 80 to 100-, 100 to 150-, and 150 to 200-mesh sizes for the preparation of filters of different porosities.

A disk of light asbestos board is cut with cork borers to fit snugly inside the glass tube, supported by a wad of asbestos fiber as indicated in Figure 1. Powdered glass, of a size selected for the purpose in hand, is poured on top of the asbestos to form a layer about 5 mm. thick. The tube is then rotated in a needle-point gas-air blast-lamp flame with the flame directed on the tube just outside the powdered glass. In a few seconds the exposed surface of the powdered glass is sintered sufficiently to permit inverting the tube. The flame is then played in the region of the asbestos until the latter acquires a brilliant flesh color.

The heating is continued for about a minute at the maximum temperature of the air-gas flame. By this time the walls of the glass tube should have acquired a stippled appearance. A little experience will show how much heating is required. It is desirable to test the sintering at this time by gently poking the surface with a wire. If it crumbles readily, it may be heated directly in the flame until it becomes firm. After suitable annealing and cooling, the asbestos is easily removed by alternately sucking air and water through the tube.

In addition to filters in straight tubes this technique can be applied (8) to the construction of gas-distribution tube (Figure 1, right). To obtain effective dispersion of a gas in a liquid, the gas must be delivered upward and the bubble size is governed not only by the pore size but also by the pressure drop across the filter and by the character of the liquid. It was expected that the smaller area of sintered glass necessitated by this method of preparation would make disks inferior to the gas-distribution disks of larger area.

It appears, however, that at moderate pressures only a few spots even on the larger disks deliver bubbles, the rest of the surface being ineffective unless the pressure is raised. Tubes prepared as described deliver gas at ordinary pressures from a number of points at a rate comparable with the tubes of larger sintered surfaces.

## Summary

Although sintered-glass filters have many applications, their use has been limited by the lack of a commercial supply in the borosilicate glass and of adequate directions and facilities for making them. This paper presents a technique for sintered-glass preparation, requiring a minimum of skill and equipment.

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# Thermostatic Bath for Low-Temperature Viscosity Determinations

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THE determination of the viscosity of liquids at low temperatures presents a number of mechanical difficulties which cannot be overcome without the use of elaborate setups. The main sources of error are due to poor temperature control and also, if a pressure instrument is used, to difficulties in maintaining constant pressure. Since the viscosity of fluids increases very rapidly with decreasing temperature, the importance of proper control of temperature is evident in order to avoid large variations in results. Moreover, such close temperature control must be maintained for such longer periods of time, particularly when using viscometers of the capillary type.

The viscosity of lubricating oils at low temperatures has been determined by a number of authors, in particular Okochi and Majima (7), Schlenker (8), Tonomura (12), Hausz and Mellner (11), Ferry and Parks (2), Tanaka, Kobayasi, Tsukuda, and Ono (10), FitzSimons (3), Ivanov and Gutzeit (5), Jordachescu (6), and Schwaiger (9). In general either no data were furnished on the accuracy of the temperature control or such control was limited to  $\pm 0.5^\circ\text{C}$ ., which is too wide a variation for precise measurements. The FitzSimons apparatus gave temperature variations not exceeding  $0.01^\circ\text{C}$ . by circulating ethyl alcohol at  $-60^\circ\text{C}$ . in a copper coil inserted in a Dewar flask containing ethyl alcohol. The desired temperature was then obtained by heating the bath with an immersion electric heater, the cur-

rent being controlled by means of a mercury thermoregulator connected to a vacuum tube relay. No description of the bath used for cooling the circulating alcohol was given.

The work of the above investigators shows that the determination of low-temperature viscosities is a fairly complicated problem. Such determinations are therefore not generally considered a part of the routine of petroleum inspection laboratories. However, special problems often require the use of viscosity data at low temperatures and to meet this demand a setup capable of furnishing accurate data at short notice was designed by the authors. This setup has been found very satisfactory and, for this reason, it should be of interest to other laboratories engaged in similar work.

## Apparatus

The apparatus shown in Figure 1 consists of three parts: cooling coil and bath, thermostatic bath, and viscometer and bath.

The cooling coil, *C*, consists of a copper coil immersed in a bath, *B*, of alcohol cooled to the desired temperature by occasional additions of solid carbon dioxide. Coil *C* is connected to the cooling coil, *D*, of a Hoeppler ultrathermostat, *H* (4), the liquid (a suitable alcohol-water mixture) being circulated by means of a small centrifugal pump, *P*.

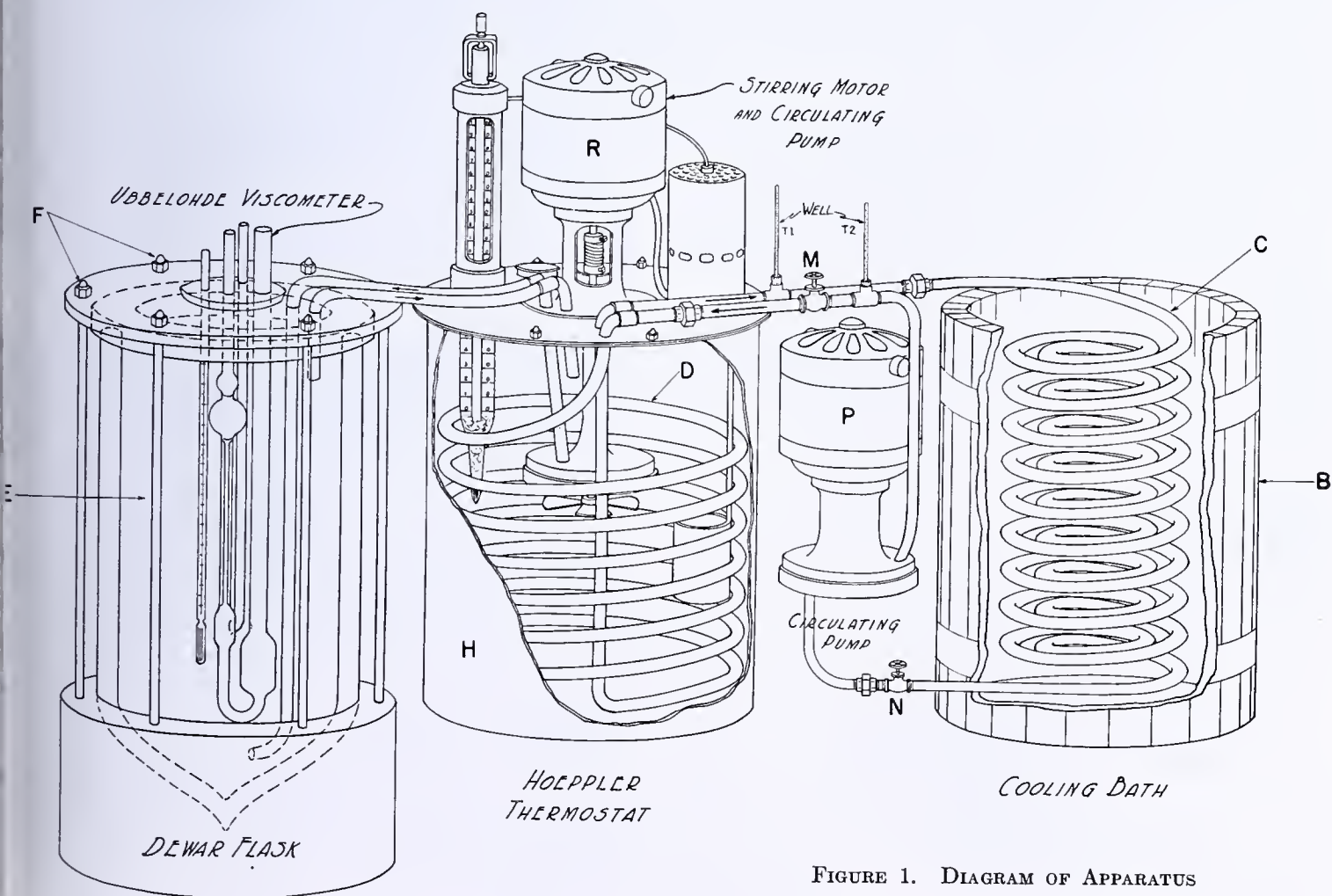


FIGURE 1. DIAGRAM OF APPARATUS



Bath *E* is an unsilvered Dewar, of 10-liter capacity, covered with a grooved hard-rubber head surmounted by a brass plate held firmly by means of the rods and bolts, *F*. A tight joint is obtained by inserting a rubber gasket in the groove of the hard-rubber head. The brass cover is provided with a tapered hole through which a Ubbelohde viscometer (13) held by a rubber cork is inserted. The viscometer is calibrated in accordance with A. S. T. M. procedure (1). Baths *B* and *H*, as well as all connecting lines, should be heavily insulated with cork in order to prevent moisture condensation.

The Hoespler falling-ball viscometer (4) can be substituted for bath *E* for temperatures above 0°, but cannot be used for temperatures much below 0°, because of frost formation on the surface of the outer jacket. For this reason, a Dewar bath is more preferable.

In carrying out a determination, bath *B* is filled with either alcohol or acetone (isopropyl alcohol being very convenient); and a suitable water-alcohol mixture is introduced through cock *M* into the cooling coil system as well as into baths *H* and *E*. The freezing point of the alcohol-water mixture must be at least 20° C. below the desired viscosity temperature. The viscometer is then inserted in bath *E*, the thermostat is plugged in, and circulation pumps *P* and *R* are started. The alcohol in bath *B* is rapidly cooled by additions of solid carbon dioxide to the desired temperature. In general, it is necessary to maintain the coil temperature about 8° to 10° C. lower than the temperature desired in bath *E* in order to obtain the best thermostatic control with the Hoespler apparatus. This can be accomplished by regulating the addition of solid carbon dioxide so as to maintain the temperature of bath *B* about 10° lower than that of the coils. Still better procedures consist of regulating the circulation rate by means of a rheostat attached to the motor, or adjusting the pressure by means of stopcocks *M* and *N*. The temperatures of the incoming and outgoing fluids are read by means of thermometers *T*<sub>1</sub> and *T*<sub>2</sub>—for example, if a temperature of -10° C. is desired in bath *E*, the coil temperature must be about -18° to -20° C. and bath *B* about -30° C.

Under the above conditions, the thermostat is capable of temperature control within  $\pm 0.03^\circ$  C. in bath *E* as read with a Leeds & Northrup Type 8662 potentiometer.

The thermostat is generally supplied with a mercury regulator for temperatures down to -25° C. For lower temperatures the authors have replaced this mercury control with a Burling metallic thermostat which has been attached to the Hoespler bath. With this thermostat temperatures as low as -52° C. have been maintained within  $\pm 0.03^\circ$  C. for hours without difficulty. The Burling thermostat used for this work was designed for temperatures of about -60° C.; it did not give such good control around -30° C., the variations being about  $\pm 0.1^\circ$ . In ordering this thermostat the temperature range must be specified for best results.

### Acknowledgment

The authors wish to express their appreciation to E. M. Fry and W. J. Troeller of these laboratories for their valuable suggestions.

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## A High-Performance Electronic Relay

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THE relay described in this paper was designed primarily for use with a mercury thermoregulator for controlling the temperature of a water bath. The requisites for this service—small control contact current to prevent deterioration of the contacts, low control contact voltage to prevent sparking and insulation breakdown (which is especially desirable because of the high humidities often encountered), simplicity, and low cost—are met to an unusual degree.

To obtain the lowest contact voltages possible in a design using one receiving type tube and but a single sturdy magnetic relay, the circuit, Figure 1, takes advantage of characteristics

of one of the new higher transconductance, "beam" type tubes and utilizes grid rectification of the control circuit voltage. It requires no source of power other than the usual 110 volt single-phase line. It is especially useful to prevent chatter of the magnetic relay under conditions of vibration because of the fact that condenser *C*<sub>1</sub> is relatively slowly charged or discharged.

Circuit A of Figure 1 is connected for use with a mercury thermoregulator (controlled circuit open when controlling circuit closed). To connect it for use with a bimetal regulator, it is necessary merely to rewire the grid circuit leads as at B.

To place the relay in operation, the strap connected to the tube cathode should be placed at about the center, and the other movable contact at the ground end of *R*<sub>2</sub>. To obtain minimal voltage across the contact point the cathode strap is first adjusted so that the relay will just open when the control terminals are shorted (or opened if the circuit is arranged as at B), then the other strap is moved towards it until the relay just closes, when the control terminals are opened. To fine an adjustment should not be attempted, since some allowance for line voltage fluctuation is necessary. When properly adjusted, the root mean square values of voltage and current across the contact points are approximately 100 volts and 0.1 milliamperes.

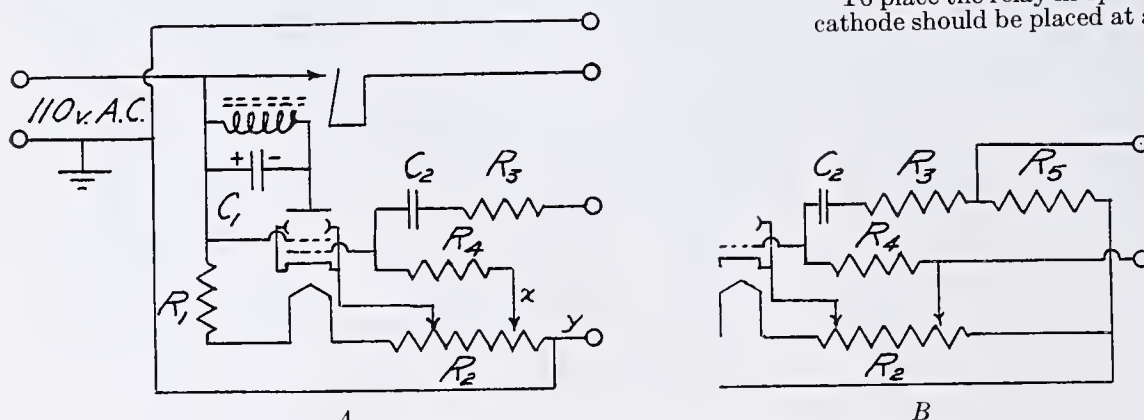


FIGURE 1. DIAGRAM OF CIRCUIT

- Tube 25L6 or 25L6-G. Relay, 3000-ohm 20-milliamperes coil, Leach No. 1201
- C*<sub>1</sub>. 8-microfarad 150-volt electrolytic, Cornell Dubilier BR No. 875
- C*<sub>2</sub>. 0.1 microfarad, paper
- R*<sub>1</sub>. 250 ohms, 50 watts; IRC PE
- R*<sub>2</sub>. 50 ohms, 10 watts; IRC PBA, with extra strap
- R*<sub>3</sub>, *R*<sub>5</sub>. 0.1 megohm, 1 watt; IRC BT-1
- R*<sub>4</sub>. 1.0 megohm, 1 watt; IRC BT-1



If the relay performs erratically, which it may if long unshielded leads go to the control contacts, the values of  $R_3$ ,  $R_4$ , and  $R_5$  may be changed to one tenth of those shown, and  $C_2$  increased in the same ratio. The current through the control contacts then becomes 0.8 milliamperes.

It is important that the grounded side of the line be connected as shown. If one side of the regulator is grounded, it must obviously be connected to the same point. A mercury regulator is preferably connected so that the lead which remains in contact with the mercury when the mercury column falls is on the grounded side. One side of a bimetal regulator, or other controller requiring the relay to make the control contacts close, may be grounded only if a break-when-energized relay is used in circuit A.

A 50-watt light globe may be substituted for  $R_1$ , but it is not recommended because the first cost is only a few cents less, and the resistor is more dependable.

If a quicker acting relay is wanted, condenser  $C_1$  may be changed to the smallest value which will keep the relay from buzzing (about 1 microfarad), condenser  $C_2$  shorted out in circuit A, and the straps readjusted on resistor  $R_2$ . With these changes the circuit becomes nearly identical with one described by Hersh, Fry, and Fenske (1), except for the use of the beam power tube and of resistor  $R_3$  to limit the current of the control grid during the part

of the cycle when it is positive with respect to the cathode. This modification is suitable for use on direct current power lines, but for alternating current use it imposes about twice the voltage across the regulator contacts for any particular plate current requirement. This circuit may be used with a bimetal regulator by interchanging the grid leads at points  $x$  and  $y$ .

The magnetic relay is rated to handle 500 watts. Should larger amounts of power be required, there is available a current of about 40 milliamperes at voltages up to 50 volts (about 20 milliamperes at 100 volts) for operation of a heavier relay, if the contact voltage may be increased to 16 volts. Condenser  $C_1$  should be as large as is practical (say, 32 microfarads) to obtain maximum power to operate the relay.

The total cost for the parts is less than \$8.00, more than half of which is for the magnetic relay. Parts are available from any radio supply house.

### Literature Cited

- (1) Hersh, R. E., Fry, E. M., and Fenske, M. R., *IND. ENG. CHEM.*, 30, 363 (1938).

## Correspondence—Determining Gold in Cyanide Plating Solutions

SIR: Kushner's article on a method for determining gold in cyanide plating solutions [*IND. ENG. CHEM., Anal. Ed.*, 10, 641 (1938)] might lead some to think that the Weisberg method there referred to was originated by me. That is not the case. The sulfuric acid decomposition method has been employed in this laboratory for a number of years. Its use here was started by William B. Stoddard, Jr.

We seldom encounter difficulty due to failure of the gold to coagulate. However, our procedure is a little different from that described by Kushner. We seldom use more than 25 ml. of sulfuric acid to effect the decomposition. The decomposition is carried out in a Kjeldahl flask. If the mixture is not overheated at the beginning, the gold can be readily coagulated by adding water after decomposition is completed and boiling the mixture for a few minutes.

LOUIS WEISBERG

WEST 45TH ST.  
NEW YORK, N. Y.  
November 28, 1938

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SIR: At the time of writing, I was aware that the method might not be original with Dr. Weisberg, but since he communicated to me, I credited him with suggesting it. If the method was initiated by Stoddard, he deserves full recognition.

Regarding the second paragraph of Dr. Weisberg's letter, the difficulty was not that the gold failed to coagulate, but that some of the finer particles of the metal failed to precipitate and remained in colloidal suspension in the sulfuric acid solution. It may have been a negligible amount, but it was almost always there. I tried varying the rate of heating, but had no success in completely eliminating the effect. Another objection to adding water after decomposition has been completed is the danger involved in adding it to hot acid.

While the Kjeldahl flask is now in use in Dr. Weisberg's laboratory, I was under the impression that an Erlenmeyer flask was employed. The long neck of the Kjeldahl is no doubt an advantage in condensing the acid vapors and conserving the sulfuric acid needed to effect decomposition. However, the sloping walls of the cone flask bring about the same result to a large degree, besides permitting easy washing and transfer of gold to the Gooch crucible.

I feel that I did not stress sufficiently the fact that fumes given off during the reaction are violently poisonous. The list of constituents of these fumes reads like a Who's Who of toxic and irritating gases. Any or all of the following may be evolved: HCN, (CN)<sub>2</sub>, CO, CO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>. The first five are given off at the beginning of the process as the sulfuric acid decomposes the cyanides, formates, and carbonates that are usually present in the plating solution, and the last gas is generated as the sulfuric acid starts to boil, just before the gold is precipitated. It is therefore very important that a good draft hood be used for the decomposition. Under no circumstances should the face be brought close to the mouth of the flask during addition of the sulfuric acid or at any time thereafter. If these precautions are taken there is no danger.

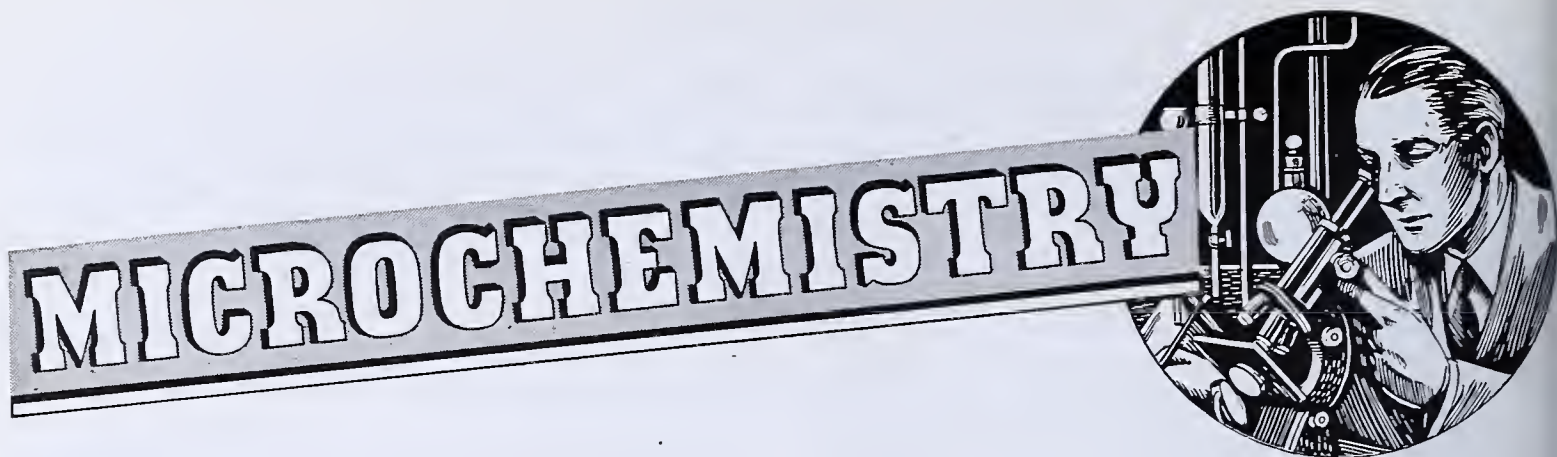
Metals of the platinum family if present will interfere. Platinum, rhodium, ruthenium, and iridium never occur in commercial gold plating solutions and need not be considered. Rarely some palladium may be found—generally in what is known as an "optical pink" gold solution. When present it precipitates partially with the gold. The gold no longer coagulates into a sponge, but comes down as a brownish black powder contaminated with palladium. In such a case, it is best to use the evaporation method (Scott, W. W., "Technical Methods of Metallurgical Analysis," pp. 718-19, D. Van Nostrand Co., New York, 1923) and the regular fire assay.

Of the more common metals, iron, if present in large quantities, also interferes. While the commercial gold plating baths of today seldom if ever contain sodium or potassium ferrocyanide, single-cell (commonly termed "salt water") gold solutions still make use of these salts. If present, they are decomposed by the sulfuric acid with the formation of ferric sulfate. Ferric sulfate, being insoluble in sulfuric acid, comes down as a grayish white powdery coating over the gold sponge. After decanting most of the sulfuric acid and carefully washing the precipitate in the flask with water, decanting repeatedly, several alternate washings with dilute sodium hydroxide and hydrochloric acid, finally ending with boiling hot water, will completely remove the ferric sulfate. The gold can then be filtered onto a Gooch crucible as previously described [*IND. ENG. CHEM., Anal. Ed.*, 10, 641 (1938).]

304 ECHO PLACE  
NEW YORK, N. Y.  
December 23, 1938

J. B. KUSHNER





# Determination of Antimony in White Metals

## A Volumetric Semimicromethod

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THE present method is an application of a dilute bromate solution, 0.005 *N*, for the determination of antimony in tin and lead and in alloys of the metals with antimony. The procedure has grown out of previous work (1), in which a more concentrated bromate solution was used on 1.5-gram samples.

The method may be used in the analysis of alloys such as hard lead, containing about 1 per cent of antimony, and tin-base bearing alloys, containing about 7 to 11 per cent of antimony. The procedure is usually applied to quantities of antimony in the range from 0.01 to 0.10 per cent in tin and lead and in solder made with the metals, and is identical in principle with that employed in the conventional method. To enable the application of 0.005 *N* bromate solution, the quantities of the reagents used have been greatly decreased. The use of pure arsenic trioxide for standardizing the bromate solution is an aid to the attainment of accurate results. The degree of precision of which the method is capable is shown by Table I, presenting data obtained in determining antimony in Bureau of Standards tin-base bearing metal, containing 7.32 per cent of antimony, and another tin-antimony alloy found to contain 10.60 per cent of antimony.

The antimony content of tin and lead tested in this labora-

tory varies over a narrow range; in tin it is seldom greater than 0.02 per cent and in lead often less than 0.01 per cent. A semimicrotip attached to the 10-ml. buret is used for titrating in the analysis of lead samples, and is an aid to attaining greater accuracy. A piece of glass tubing, 5 to 6 mm. in diameter, is drawn out to nearly capillary size, is attached to the buret by rubber tubing, and should deliver about 4 drops for 0.05 ml. of bromate solution.

Antimony determinations on tin samples, and tin-antimony and lead-antimony alloys can be performed in less than 1 hour; on lead and solder samples in 1.5 to 2 hours.

### Reference Standards

Bureau of Standards samples 42b and 54A were used as reference standards in the development of this method. The antimony content of the tin sample, No. 42b (Table II), is 0.018 per cent. This is in close agreement with the value 0.02 per cent, assigned to the sample when the former work was in progress.

The tin-base bearing alloy, No. 54A, contains tin 88.61, antimony 7.32, copper 3.75, lead 0.21, iron 0.041, arsenic 0.039, and bismuth 0.019 per cent. Experimental analyses with this sample (Table I) show the antimony content to be 7.31 per cent.

Bureau of Standards arsenic trioxide, sample 83, with a purity of 99.98 per cent, is used for standardizing the bromate solution. Metallic antimony, often used for standardizing solutions of the salt, is difficult to obtain in the pure form. Samples of antimony tested show the presence of arsenic and silica. Potassium bromate is obtainable in a highly purified form. When solutions of the salt have been standardized by means of arsenic trioxide, the values obtained have always been in very close agreement with the theoretical, making the application of a correction factor unnecessary.

TABLE I. DETERMINATIONS ON TIN-ANTIMONY AND LEAD-ANTIMONY ALLOYS

Sample	Weight of Sample Gram	0.005 <i>N</i> KBrO <sub>3</sub> Ml.	Antimony Originally Present Mg.	Antimony Added Mg.	Total Antimony Present Mg.	Antimony Found Mg.	Error Mg.	Recovery %
Bureau of Standards Sample 54A, tin-base bearing metal	0.01	2.40	0.732	...	...	0.731	-0.001	99.9
	0.01	5.60	0.732	1.00	1.732	1.705	-0.027	98.4
	0.01	5.05	0.732	0.80	1.532	1.537	-0.005	100.3
	0.02	4.80	1.464	...	...	1.461	-0.003	99.8
	0.02	4.75	1.464	...	...	1.446	-0.018	98.7
	0.02	7.65	1.464	0.875	2.339	2.329	-0.01	99.6
	0.02	7.75	1.464	0.90	2.364	2.359	-0.005	99.8
Another tin-antimony alloy	0.01	3.50	...	...	...	1.065	.....	....
	0.01	3.45	...	...	...	1.05	.....	....
	0.01	3.50	...	...	...	1.065	.....	....
	0.01	3.50	...	...	...	1.065	.....	....
	0.02	6.95	...	...	...	2.116	.....	....
	0.02	6.95	...	...	...	2.116	.....	....
	0.02	8.35	2.116	0.425	2.541	2.542	+0.001	100.04
	0.02	8.95	2.116	0.625	2.741	2.724	-0.017	99.4
Lead-antimony alloy	0.02	9.25	2.116	0.70	2.816	2.815	-0.001	99.96
	0.20	8.00	...	...	...	2.435	.....	....
	0.10	4.15	...	...	...	1.263	.....	....
	0.10	4.10	...	...	...	1.248	.....	....
	0.10	4.10	...	...	...	1.248	.....	....
	0.10	4.10	...	...	...	1.248	.....	....
	0.10	7.35	1.248	1.00	2.248	2.237	-0.011	99.5
	0.10	6.55	1.248	0.75	1.998	1.994	-0.004	99.8
	0.10	8.95	1.248	1.50	2.748	2.724	-0.024	99.1



TABLE II. ANALYSES OF TIN AND SOLDER							
(Using 0.6-gram samples)							
Sample	0.005 N	Antimony	Antimony	Total	Antimony	Error	Recovery
	KBrO <sub>3</sub>	Originally	Added	Antimony	Found		
	Ml.	Mg.	Mg.	Mg.	Mg.	Mg.	%
Antimony	4.90	...	1.50	...	1.492	-0.008	99.5
	4.95	...	1.50	...	1.507	+0.007	100.5
	3.90	...	1.20	...	1.187	-0.013	98.9
Bureau of Standards tin sample 42b	0.35	...	0.65	...	0.107	...	...
	2.50	0.107	0.65	0.757	0.761	+0.004	100.5
	3.30	0.107	0.90	1.007	1.005	-0.002	99.8
Tin sample, Cempure, from International Tin Research & Development Council, London Continental Can Co.	0.35	...	...	...	0.107	...	...
	3.00	0.107	0.80	0.907	0.913	+0.006	100.7
	4.45	0.107	1.25	1.357	1.355	-0.002	99.8
	0.25	...	...	...	0.076	...	...
	No. 1	2.30	0.076	0.63	0.706	-0.006	99.1
	No. 2	0.40	...	...	0.122	...	...
		2.85	0.122	0.75	0.872	-0.004	99.5
	No. 3	0.50	...	...	0.152	...	...
		3.10	0.152	0.80	0.952	-0.008	99.2
					0.944	-0.008	99.2
Solder samples from Mount Royal Metal Co., Canada	0.15	...	...	...	0.046	...	...
	2.10	0.046	0.60	0.646	0.639	-0.007	99.0
	No. 2	1.05	...	...	0.32	...	...
		3.85	0.32	0.85	1.17	+0.002	100.2
	No. 3	1.35	...	...	0.411	...	...
	2.10	0.411	0.225	0.636	0.639	+0.003	100.5

**Solutions and Reagents Required**

**Bromine Solution.** Dissolve 12 ml. of pure bromine in 100 ml. of concentrated hydrochloric acid by shaking vigorously in a glass-stoppered bottle.

**Methyl Orange Indicator.** Dissolve 0.10 gram of methyl orange powder in 100 ml. of hot water and filter.

**Anhydrous Sodium Sulfite.**

**Potassium Bromate Solution, 0.005 N;** 1 ml. = 0.3044 mg. of antimony. Weigh 0.1392 gram of the salt, dissolve in water, and make up to volume in a liter flask. Standardize against pure arsenic trioxide. Weigh a quantity of the trioxide, 4.95 mg., then dissolve in 1 drop of a saturated solution of sodium hydroxide. Add a few milliliters of water and 1 ml. of concentrated sulfuric acid, and titrate as in the regular analysis. The quantity of bromate required in this titration is 20 ml. after deducting the reagent blank correction, 0.15 ml.

Procedure for Tin, Lead, and Solder

Weigh a 0.6-gram sample of filings, 80-mesh for lead, into a 50-ml. beaker. Add a few milliliters of concentrated hydrochloric acid and about 5 ml. of the bromine-hydrochloric acid solution. Heat over a small flame, adding small quantities of bromine solution as required to complete solution of the metal. At this stage in the process, the solution should appear pale yellow in color, indicating a slight excess of free bromine. The presence of any considerable amount of free bromine upon solution of the metal may prevent suitable reduction of the antimony by sodium sulfite.

Add to the hot solution 20 mg. of anhydrous sodium sulfite, followed by 5 ml. of concentrated hydrochloric acid, and evaporate to a volume of 7 to 8 ml. to expel any arsenic present. Add 1 ml. of concentrated hydrochloric acid and 5 ml. of water and place over the small flame again until gentle boiling begins. Pass a gentle current of air through the solution for 30 seconds. Remove from the burner, wash off the cover glass and sides of the beaker, and titrate with 0.005 N potassium bromate solution, using a 10-ml. buret graduated in 0.05-ml. divisions. After the addition of a drop of methyl orange indicator add the bromate solution drop by drop to the disappearance of the pink color of methyl orange. During the titration keep the temperature of the solution near the boiling point. The high temperature aids in obtaining a more distinct end point. From the final buret reading deduct 0.15 ml., the amount obtained in the titration of a blank

run under the conditions obtaining in this determination. It is advisable to determine the reagent blank correction occasionally. The amount of this correction may vary according to the purity of the reagents used.

Procedure for Tin-Antimony and Lead-Antimony Alloys

Analyses of these alloys are performed with 0.10-gram samples of 80-mesh filings for lead-antimony alloys, and 0.02-gram samples for tin-antimony. To these quantities add 5 to 10 ml. of concentrated hydrochloric acid, using 50-ml. beakers, and heat gently over a small flame for 5 to 10 minutes. At this stage some of the antimony, separated in black powdery form, can be observed on the bottom of the beaker. Add a few drops of bromine-hydrochloric acid solution which has

been diluted with about 2 volumes of concentrated hydrochloric acid. Heat over the flame, adding a few drops of bromine solution as required, to complete solution of the antimony, avoiding more than a slight excess of bromine. Upon addition of 35 to 40 mg. of sodium sulfite, the process is continued as in the procedure for tin, lead, and solder.

In the first three experiments of Table II, quantities of antimony, taken from a solution prepared by dissolving powdered antimony in concentrated hydrochloric acid with the addition of potassium chlorate, were carried through the regular course of analysis. In all the experimental analyses of Tables II and III, the error is less than the antimony value of 0.05 ml. of the bromate solution.

TABLE III. ANALYSES OF LEAD							
(Using 0.6-gram samples)							
Sample	0.005 N	Antimony	Antimony	Total	Antimony	Error	Recovery
	KBrO <sub>3</sub>	Originally	Added	Antimony	Found		
	Ml.	Mg.	Mg.	Mg.	Mg.	Mg.	%
Continental Can Co. lead samples	0.20	...	...	...	0.061	...	...
	0.20	...	...	...	0.061	...	...
	3.50	0.061	1.00	1.061	1.065	+0.004	100.4
Sample 2	0.15	...	...	...	0.046	...	...
	2.10	0.046	0.60	0.646	0.639	-0.007	99.2
Sample 3	0.10	...	...	...	0.03	...	...
	1.45	0.03	0.42	0.45	0.441	-0.009	98.0
Sample 4	0.05	...	...	...	0.015	...	...
	2.35	0.015	0.70	0.715	0.715	...	...

The antimony content of the second tin-antimony alloy shown in Table I was found to be 10.60 per cent, the average of several determinations. The third and fourth experiments using 0.01-gram samples, and the fifth and sixth, in which 0.02 gram was used, were carried out consecutively. The average value for the antimony content obtained in these four analyses is 10.61 per cent. The average value obtained in the six experimental analyses, determining the antimony content of this alloy, is 10.60 per cent.

Literature Cited

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# Analytical Balances in Quantitative Microanalysis

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Many analytical balances possess precisions ranging from  $\pm 10$  to  $\pm 50$  micrograms and can be used as substitutes for microchemical balances in the performance of quantitative microanalyses. The method of weighing developed by Bunge and Kuhlmann (8), which is employed with microchemical balances, is recommended for general use with analytical balances; the calculated deflection is explained as that ideal deflection which would be directly observed, if it were possible to free the method of single deflection (3) from manipulatory distortions.

The question of the minimum size of sample required for attaining a specified precision of the analytical result is treated mathematically. The results are summarized in Table I in a form which permits their practical application without making it necessary to refer to the details of the theoretical discussion. It is hoped that the possibility of employing analytical balances will assist in spreading the use and teaching of quantitative microchemical procedures.

PREGL performed the first series of his investigations on the feasibility of microprocedures for the quantitative elementary analysis of organic substances, using an assay balance (4) whereby the weights were determined to the nearest hundredth milligram (12, 13). Later the use of sensitive analytical balances was repeatedly suggested (2, 7, 11, 14, 15, 16), and semimicromethods were recommended with the intention of evading the exacting requirements for the precise determination of mass with the microchemical balance. The possibility of enlisting analytical balances in the service of microanalysis may be of interest to industrial and commercial laboratories, and may facilitate the spreading of instruction in quantitative micromethods which often must be limited to a few promising students for lack of a sufficient number of microchemical balances. In consideration of these possible benefits, but with no intention of denying the superiority of microchemical balances, the following discussion attempts to prove that precise analytical balances may be employed not only in semimicroanalysis, but also in the performance of certain determinations on milligram samples. In addition, the range of applicability of such balances in the field of quantitative micromethods is clearly defined.

## Method of Weighing

The method of short swings combined with the calculation of the deflection is recommended for all precise work with analytical balances operated without damping devices. The time required for a weighing compares favorably with that needed when using a damped balance, and the precision with the swinging balance should be somewhat better than that obtained when reading the equilibrium position of the pointer with the balance at rest.

The procedure of weighing is described in the microchemical literature (5, 10) and may be applied to analytical balances as follows:

When the approximately correct weight has been found by preliminary trial, the rider is brought as exactly as possible into position, so that it appears from the front as one perpendicular line coinciding with the selected division of the rider scale. There is no reason, with analytical balances to use any other divisions of the rider scale but those corresponding to a whole number of milligrams. In releasing and arresting the balance the functioning of the arresting mechanism of the microchemical balances, and analytical balances of European make, is copied—i. e., the beam is released last and arrested first, contrary to the usual American practice with balances having a separate pan-arresting mechanism. The first two complete swings are discarded and the following three consecutive points of inflection are read, counting the divisions of the pointer scale as tens and taking the center of the scale as zero—e. g., left  $-11$ , right  $+30$ , left  $-9$ . The deflection is calculated by averaging the two readings on one side of the swing,  $\frac{1}{2}(-11 - 9) = -10$ , and algebraically adding the result to the reading on the other side of the swing,  $-10 + 30 = +20$ .

The deflection may be defined as the other point of inflection of an ideal swing having zero for one point of inflection. In the example cited above, the points of inflection of such a swing would be 0 and  $+20$ . It is obvious that the needle would point to  $+10$  when the swing dies down and the balance is at rest or, generally speaking, that the deflection is equal to twice the rest point. The use of the deflection (*Ausschlag*), also referred to as "deflection difference" (5) or "deflection sum" (10) in the American literature, originated with Paul Bunge and Kuhlmann (8) who adjusted the sensitivity of their balances so that the use of the deflection led to simple figures for the sensitivity, 0.1 or 0.01 mg. per division of the pointer scale. The usual objection to their procedure of evaluating the swing of the balance is that the deflection has no physical meaning. This, of course, is not justified. An attempt at direct observation of the deflection is made in the "single deflection method" described by Brinton (3) where the balance is adjusted and released in such a way as to permit the pointer to perform a nearly perfect swing starting at the zero division of the pointer scale. Only the first point of inflection is read and is considered as the deflection. It is obvious that the procedure of Bunge and Kuhlmann for the calculation of the deflection from observations on the free swinging balance must give more reliable results.

The sensitivity is determined by shifting the position of the rider for a distance corresponding to a change in weight of mg. and determining the deflection, which now might be  $-57$ . The sensitivity is calculated as the fraction, "change of mass over change of deflection":

$$\frac{1 \text{ mg.}}{+20 - (-57)} = 0.013 \text{ mg. per unit of the pointer scale.}$$

The evaluation of the observed deflections in terms of milligrams is performed in the usual way by multiplying the deflection by the sensitivity. Thus the deflections quoted in the examples correspond to the masses:

$$\begin{array}{r} 20 \times 0.013 = 0.26 \text{ mg.} \\ 57 \times 0.013 = 0.74 \text{ mg.} \\ \hline 1.00 \text{ mg.} \end{array}$$

The sum, 1.00 mg., corresponds to the mass represented by the displacement of the rider. Generally one may say that the deflection is converted into mass by use of the formula

$$\text{Mass} = \text{deflection} \times \text{sensitivity} = \text{deflection} \times \frac{1 \text{ mg.}}{\text{deflection change}}$$



This equation shows clearly the futility of calculating the rest point. Since the latter is one half of the deflection, the formula shows that the user of the rest point is amusing himself by dividing by two the numerator and denominator of a fraction.

As to the general procedure of weighing, treatment of balance, and selection of balance room, the customary precautions (5, 10) should be more closely approximated the higher the precision needed. If the precision of the weighings is to be  $\pm 0.01$  mg. or better, it becomes advisable to keep the temperature of the balance room reasonably constant and to eliminate changes of the buoyant effect by the use of tares of suitable density.

### Determination of Precision of Balance

The determination of the average deviation of a single weighing has been described (1); it appears advisable to base the calculation on the results of a series of at least ten weighings, and to verify the precision by redetermination at reasonable time intervals. The manufacturers' specifications on the "sensitivity" of their balances usually do not permit conclusions concerning the precisions obtainable but in general the efficiency of analytical balances is very gratifying, a fact which has been known for a long time. Felgentraeger (6) predicted in 1907 that the precision of a correctly constructed balance could be one thousandth of the weight of the rider. Manley (9) tested a balance with a beam of Invar steel and determined average deviations of a few micrograms or weighings with loads from 0 to 200 grams. Analytical balances and "semimicrobalances" of a "sensitivity" of 0.01 mg. are offered by American and European manufacturers. Inexpensive students' balances of American manufacture, tested after 3 and 5 years of use, showed average deviations ranging from 0.005 to 0.05 mg. (1). Finally, the inherent stability of the correctly constructed analytical balance for the attainment of high precision is also suggested by the fact that the modern microchemical balance is essentially a reproduction of Kuhlmann's assay balance (4) which, in turn, is a small-scale model of his analytical balance with constant sensitivity from zero to maximum load (200 grams).

### Calculation of Required Amount of Sample

The percentage,  $P$ , of constituent  $X$ , as calculated from the measurements of a quantitative determination, is directly proportional to the measure,  $M$ , of  $X$  (mass of the weighing form, volume of standard solution, etc.) and inversely proportional to the mass,  $S$ , of the sample. Therefore, the relative precision,  $\pi'$ , of the result,  $P$ , is determined as follows by the relative precisions,  $\mu'$  and  $\sigma'$ , of  $M$  and  $S$  (1):

$$\pi' = \pm \sqrt{\mu'^2 + \sigma'^2} \quad (1)$$

While in general the error,  $\mu$ , of the measure,  $M$  (weight of the precipitate, volume of standard solution or gas), is determined by the shortcomings of the "chemical" procedure to such a degree that the weighing error becomes insignificant, in the present case, where the balance is utilized to the limit of its efficiency, the conditions are exactly reversed. Thus, if the employing of analytical balances is coupled with the use of proper, truly microchemical procedures, it may be justly assumed that the precision of the result will be influenced solely by the determinations of mass.

In chemical work the mass of a substance is always determined from the difference of two weighings, even if the material be placed directly on the pan of the balance, and it appears that every determination of mass is affected by the errors of two weighings. The average deviation of the difference of two weighings of the precision,  $\omega$ , is now equal to  $1.4 \omega$  (1), and this quantity is to be considered as the absolute average

deviation of any analytical determination of mass performed with a balance giving the average deviation,  $\omega$ , in a single weighing.

The relative average deviation of the determination of any weight,  $W$ , may be calculated as follows (1):

$$\omega' = 1000 \frac{1.4 \omega}{W} \% \text{ (parts per 1000 parts)} \quad (2)$$

The equation shows that the relative precision,  $\omega'$ , may be adjusted by a proper variation of  $W$ , but, as a rule, the relative error,  $\omega'$ , is determined by the precision requirements of the analytical work and the minimum weight,  $W$ , of the substance is thus fixed as a function of  $\omega'$  and  $\omega$ .

$$W = 1000 \frac{1.4 \omega}{\omega'} \quad (3)$$

Usually, analysts prefer to specify the required relative precision as the largest permissible deviation—e. g., "the results are expected to check within 10 parts per 1000 parts of the determined constituent." In accordance with this custom the relative average deviation,  $\omega'$ , may be replaced by the relative maximum deviation,  $\omega'_m$ , by substituting  $1/4 \omega'_m$  for  $\omega'$  in Equations 2 and 3.

$$\omega'_m = 5600 \frac{\omega}{W} \quad (4)$$

and

$$W = 5600 \frac{\omega}{\omega'_m} \quad (5)$$

If a specified maximum deviation,  $\omega'_m$ , is not to be exceeded, Equations 4 and 5 indicate that the amount of material weighed at any stage of a quantitative determination must not be less than  $W$ . This statement is sufficient for all analyses in which only one determination of mass is required. Additional restrictions become necessary if more than one weighing is included in the computation of the result,  $P$ . The following possibilities may be considered: (1) The balance is used for the weighing of the sample only, (2) the sample and the isolated constituent,  $X$ , are weighed, and (3) the balance is used for the weighing of the isolated constituent only.

**BALANCE USED FOR WEIGHING OF SAMPLE ONLY.** In all those analyses where the determination of  $X$  is carried out by titrimetric, gas volumetric, colorimetric, nephelometric, etc., methods, the balance is required for the weighing of the sample only. Provided that the precision of the measure of  $X$  is high, the maximum error of the result,  $P$ , becomes practically equal to the maximum deviation of the weight,  $S$ , of the sample. From Equations 1 and 4 follows:

$$\pi'_m = \sigma'_m = 5600 \frac{\omega}{S}$$

and the minimum mass of the sample is consequently

$$S = 5600 \frac{\omega}{\pi'_m} \quad (6)$$

a simple function of the permissible maximum deviation of the result.

**BALANCE USED FOR DETERMINATION OF MASSES OF SAMPLE AND WEIGHING FORM.** A large number of the gravimetric determinations actually performed belong in this group.

The discussion must be broken up into four sections, since the effect of the weighing error,  $\pm 5.6 \omega$ , on the relative precision varies with the magnitude of the mass determined, and the mass,  $M$ , of the weighing form may be larger or smaller than the mass,  $S$ , of the sample, depending upon the content of these two substances on determined constituent  $X$ . If the procedures are properly executed, sample and weighing form



contain the same absolute amount of determined constituent,  $X$ . Consequently, the masses,  $S$  and  $M$ , of sample and weighing form must be inversely proportional to their percentages on  $X$ ,  $P$ , and  $100f$ , respectively. Since the approximate percentage,  $P$ , is usually known and the "chemical factor for the calculation of gravimetric determinations,"  $f$ , can be found in generally available tables, the following subsections have been arranged in accordance with the relative magnitudes of  $P$  and  $100f$ .

1. *100f is equal to or smaller than  $\frac{1}{2}P$ .* The mass,  $M$ , of the weighing form is twice or more than twice as large as the mass,  $S$ , of the sample. The square of the relative precision  $\mu'$  of  $M$  can be neglected in Equation 1

$$\pi'_m = \sigma'_m$$

and the precision of the result depends upon the precision  $\sigma'_m$  of  $S$  only. The minimum mass of sample is given by Equation 6.

2. *100f is greater than  $\frac{1}{2}P$  and smaller than or equal to  $P$ .* The masses,  $M$  and  $S$ , are approximately equal, and  $M$  is never smaller than  $S$ . Therefore, the relative deviation  $\mu'$  is approximately equal to  $\sigma'$ , but never exceeds it. It is safe to substitute the value  $\sigma'$  for  $\mu'$  in Equation 1.

$$\pi'_m = \pm \sqrt{2\sigma'^2_m} = \pm 1.4 \sigma'_m$$

Consideration of Equation 4 shows that

$$\pi'_m = 7800 \frac{\omega}{S}$$

and the required minimum mass of sample becomes

$$S = 7800 \frac{\omega}{\pi'_m} \tag{7}$$

3. *100f is greater than  $P$  but smaller than  $2P$ .* The masses,  $M$  and  $S$ , differ little, but  $M$  is always smaller than  $S$ :  $\mu'$  is slightly greater than  $\sigma'$ , and it is preferable to substitute  $\mu'_m$  for  $\sigma'_m$  in Equation 1.

$$\pi'_m = 1.4 \mu'_m = 7800 \frac{\omega}{M}$$

Substitution for  $M$  in the simple relation (1)

$$P = \frac{100fM}{S}$$

gives the minimum mass of the sample as

$$S = 7800 \frac{\omega}{\pi'_m} \times \frac{100f}{P} \tag{8}$$

4. *100f is equal to or greater than  $2P$ .*  $S$  is considerably greater than  $M$ :  $\sigma'^2$  becomes insignificant when compared with  $\mu'^2$  in Equation 1

$$\pi'_m = \mu'_m = 5600 \frac{\omega}{M}$$

and the minimum mass of sample becomes

$$S = 5600 \frac{\omega}{\pi'_m} \times \frac{100f}{M} \tag{9}$$

It is obvious that whenever  $M$  is smaller than  $S$ , sections 3 and 4, mass  $M$  must be kept above a minimum value which is determined by  $\omega$  and  $\pi'_m$ . The factor  $\frac{100f}{P}$  adjusts the size of the sample so as to keep  $M$  at this minimum value.

**BALANCE USED FOR DETERMINATION OF THE MASS OF ISOLATED CONSTITUENT ONLY.** In this group belong gravimetric determinations on gases and liquids which are measured without the use of the balance. Most examples are found in the analysis of aqueous solutions.

Only the precision,  $\mu'$ , of the determination of the mass,  $M$ , needs to be considered. The equation for the calculation of the required minimum volume,  $S$ , of the sample becomes identical with Equation 9, providing that proper dimensions for  $S$ ,  $P$ , and  $\omega$  are chosen.

## Conclusion

Equations 6, 7, 8, and 9 show that analytical balances of a precision not worse than  $\pm 0.05$  mg. can be used rather generally in quantitative microanalysis, if the requirements concerning the precision of the results are not too exacting. A relative maximum deviation of 20 parts per 1000 parts of the determined constituent could be considered adequate. It certainly suffices in those instances where the determinations are carried out for the purpose of the acquisition of microchemical technique.

The amounts of samples required to satisfy the requirement of a maximum deviation,  $\pi'_m$ , of 20‰ may be calculated by the use of Table I. In all those determinations where the

TABLE I. SIZE OF SAMPLE AS FUNCTION OF AVERAGE DEVIATION OF A SINGLE WEIGHING

The acceptable maximum deviation is chosen as 20‰ of the result,  $P$ . Since the size of the sample,  $S$ , and the precision of the determination are inversely proportional, the values of  $S$  required for any other specified maximum deviation may be easily calculated from the values of  $S$  computed from this table.

$f$  is the chemical factor for the calculation of gravimetric analyses and is found in generally used tables.

$\omega$  is to be given in milligrams; its determination is described in an earlier paper (1).

$P$  is to be given in the dimension "per cent," if the sample is to be weighed, and in "gram per liter," if the sample is to be measured.

$S$  is obtained in milligrams for weighing, and in cubic millimeters for measuring.

	Balance Used for Determination of Mass of:—					
	Sample Only	100f smaller than or equal to $\frac{1}{2}P$	100f between $\frac{1}{2}P$ and $P$	100f between $P$ and $2P$	100f equal to or greater than $2P$	Weighing Form Only
$S$ to be made equal to or greater than	$300\omega$	$300\omega$	$400\omega$	$400\omega \frac{100f}{P}$	$300\omega \frac{100f}{P}$	$300\omega \frac{100f}{P}$

balance is used for the weighing of the sample only, or where  $P \geq 200f$ , the minimum weight of the sample depends upon the precision of the balance only. In this group belong, aside from volumetric determinations, many of the gravimetric procedures which are widely used as students' experiments: the determination of chloride ion as silver chloride in sodium chloride, the determination of sulfate ion as barium sulfate in potassium sulfate, the determination of sulfur as barium sulfate in pyrite, the determination of phosphorus pentoxide as magnesium-ammonium phosphate hexahydrate in apatite and the determination of calcium oxide as calcium oxalate monohydrate in calcium carbonate or high-grade limestone. All these determinations may be carried out on a milligram scale, if the average deviation of a single weighing does not exceed  $\pm 0.02$  mg.; with this precision of the balance 6 to 8 mg. of the sample are required. The corresponding figures are 15 and 20 mg., if the average deviation of a single weighing is equal to  $\pm 0.05$  mg.

Whenever  $P$  is smaller than  $100f$ , the amount of sample must be increased by  $100f/P$  so as to keep the mass,  $M$ , of the weighing form equal to 300 or 400  $\omega$ . In all the examples of Table II, the mass,  $M$ , of the weighing form is either 6 or 15 mg., depending upon the precision assumed for the balance. Table II shows that those determinations in which the determined substance is weighed as such, as in ash determinations and electrolytic precipitations, require large samples. That the analysis of substances containing little of the determined constituent requires large samples, is common knowledge. The last example of Table II shows, however, that a small chemical factor of the weighing form is able to counteract the effect of a low content of the material in question.

As to the precision obtained in the results of actual analyses, one must not expect that the maximum deviation  $\pi'_m$



TABLE II. SIZE OF SAMPLE AS FUNCTION OF COMPOSITION OF ANALYZED MATERIAL AND WEIGHING FORM  
100*f* is greater than *P*. Acceptable maximum deviation is chosen as 20% of *P*

Type of Determination	<i>P</i> %	<i>f</i>	<i>S</i>	
			$\omega = \pm 0.02 \text{ mg.}$ <i>Mg.</i>	$\omega = \pm 0.05 \text{ mg.}$ <i>Mg.</i>
K as K <sub>2</sub> SO <sub>4</sub> in KHC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	20.8	0.449	12	30
Cu electrolytically in CuSO <sub>4</sub> ·5H <sub>2</sub> O	25.5	1	24	60
SiO <sub>2</sub> as SiO <sub>2</sub> in a silicate	30	1	18	45
Ni as dimethylglyoxime in steel	4	0.203	30	75
	<i>G./l.</i>		<i>Cu. mm.</i>	<i>Cu. mm.</i>
Cl as AgCl in sea water	20	0.247	7.5	19
P as phosphomolybdate in serum	0.2	0.016	48	120

will occur frequently. Assuming proper manipulative technique, the deviation of the results will be less than  $\pi'_m$  in more than 99.5 per cent of the determinations, less than  $\frac{1}{2} \pi'_m$  in more than 80 per cent, and less than  $\frac{1}{4} \pi'_m$  in more than 50 per cent of the determinations. The average deviation of a single weighing seems to be a constant of a properly constructed balance and, apparently, does not change unless the instrument is abused or becomes worn out as the natural consequence of years of service. Since the cleaning of a balance is more liable to upset the characteristics of the instrument than any other operation of the normal use, it may be mentioned that Rolf Paulson determined the average deviation of an American balance which had been used by students for years and, during the vacation months, had acquired a coating of dust. Computation of the results of ten weighings furnished an average deviation  $\omega = \pm 28$  micrograms. Without special care, the balance was then transferred to another floor and underwent a thorough cleaning by the expert hands of Victor Niederl. Finally R. H. Nagel undertook a redetermination of the precision of a weighing and calculated  $\omega = \pm 34$  micrograms from the results of thirty weighings. The weighings with the balance in question are seriously af-

fected by changing the positions of the masses on the pans which is obviously caused by lack of flexibility in the pan suspensions. Nevertheless, the precision appears reproducible within satisfactory limits, if care is taken to simulate closely, in determining the precision, the conditions of actual weighings. Experimental proof of the correctness of the predictions of Table I does not appear necessary. Residue determinations by the author and experiences in the laboratory of J. B. Niederl so far fully support the mathematical deductions.

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# A Modified Pregl Spiral Tube

## For Sulfur and Halogen Determinations

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THE Pregl spiral combustion tube (4) makes it necessary to remove the platinum catalysts before the combustion products can be washed out, and to dry the tube before the catalysts can again be inserted. It was thought that if the tube were cut and a ground-glass joint made of the two parts, the section could be removed to wash out the products of combustion, and the other retained in the furnace with the platinum catalysts. Such a tube was made and has been used with success in this laboratory. Hallett (2) has devised a quartz tube which does not have to be removed from the furnace. The time saved using the

tube described in this article is about the same as that saved by the use of Hallett's apparatus.

Procedure

A Pregl spiral combustion tube 640 mm. long is cut 20 mm. from the indenture. A ground-glass joint is made at that point, not by fusing one on, but by grinding on the ends of the two sections. Section B is placed in the split-type electric furnace (Fisher), so that the joint protrudes beyond the end. The sample is then introduced and oxygen admitted. Section A, containing the absorbing medium, is attached to section B without lubricant, and the tube is pulled back so that the joint is inside the furnace. This step ensures collecting the products of combustion in section A. After the combustion, the joint is pushed outside the furnace and left to cool for 2 or 3 minutes. Section A is removed and allowed to cool to room temperature, and the products of combustion are washed out.

The analyses for sulfur were made according to Saschek, (5) but water, instead of hydrogen peroxide, was used as the absorbing medium. Saschek's technique with the crucible (1), filter stick (3, 6), and small amounts of wash liquid was adapted, for the first time, to the gravimetric determination

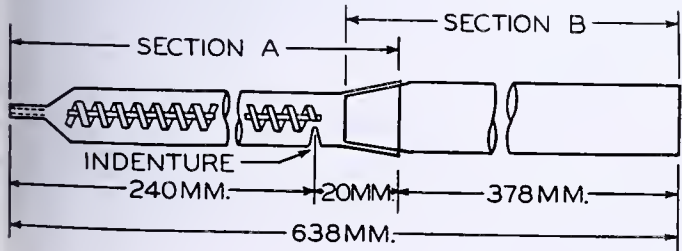




TABLE I. TYPICAL RESULTS

	Sulfur Calcd. %	Sulfur Found %		Chlorine Calcd. %	Chlorine Found %
Methionine, $C_5H_{11}O_2NS$	20.50	20.46	2-Hydroxy-4,5,6-trimethoxy- $\alpha$ -chloroaceto- phenone, $C_{11}H_{13}O_5Cl$	13.55	13.34
2-( <i>N</i> -methylamino)- <i>d</i> -camphane-10-sulfonic acid, $C_{11}H_{21}O_3NS$	12.98	12.95		Bromine Calcd.	Bromine Found
<i>p,p'</i> -Dibromodiphenyldisulfide, $C_{12}H_8Br_2S_2$	17.03	16.97	1-(4-Bromophenyl)-2,2-diphenylethanol, $C_{20}H_{17}OBr$	22.66	22.70
<i>N</i> -( <i>n</i> -amyl)- <i>m</i> -nitrobenzenesulfonanilide, $C_{17}H_{20}O_4N_2S$	9.19	9.22	<i>p</i> -Bromoacetanilide, $C_8H_8ONBr$	37.38	37.51
<i>p</i> -Carbethoxymaminobenzenesulfonamide, $C_9H_{12}O_4N_2S$	13.11	12.95	<i>m</i> -Hydroxy- <i>m'</i> -(10-bromo- <i>n</i> -decyloxy)-diphenyl, $C_{22}H_{29}O_2Br$	19.75	19.91
	Chlorine Calcd.	Chlorine Found		Iodine Calcd.	Iodine Found
Methyl- $\alpha$ -chloro- <i>p</i> -toluate, $C_9H_9O_2Cl$	19.25	19.15	Methyl-3-iodoanisate, $C_9H_9O_3I$	43.48	43.41
<i>p</i> -Chlorobenzaldehyde, $C_7H_5OCl$	25.26	25.12	<i>o</i> -Iodobenzoic acid, $C_7H_5O_2I$	51.21	51.04
5-Chloro-7-nitroisatoic anhydride, $C_8H_3O_5N_2Cl$	14.64	14.64			
<i>o</i> -Methylallothreoninebetainehydrochloride, $C_8H_{13}O_3NCl$	16.98	16.95			

of the halogens. The substitutions made in Saschek's procedure were as follows: The spiral was moistened with a saturated solution of hydrazine sulfate, dilute nitric acid (1 to 300) was used as the wash liquid, 1 cc. of 5 per cent silver nitrate was used to precipitate the halogen ion, and the crucible containing the filter stick and silver halide was dried at 120° C.

Typical results from about fifty analyses made with the tube are reported in Table I.

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## Apparatus for Microanalysis of Gas

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This article describes modern refinements of apparatus and technique for the rapid analysis of minute amounts of gas. On samples of 5 to 25 cu. mm. at normal temperature and pressure, analyses may be made with errors for each component within 2 per cent of the total sample. The errors are within 5 per cent on quantities of gas as small as the proverbial limit of 1 cu. mm. The methods described are available for the gases water, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane. One hour is required for a complete general analysis. Under special conditions the least detectable quantity of a component may be pushed to a limit of 0.025 cu. mm., equivalent to the carbon monoxide in 1 sq. cm. of a monomolecular film.

IN CONNECTION with contemporary work on the correlation between thermionic activity and the free alkaline earth metal content of an oxide-coated filament (3) the authors have had the problem of assaying extremely small amounts of active metal. This was accomplished by oxidation with carbon dioxide and analysis of the gaseous reaction products, computing active metal from the equivalent carbon monoxide formed.

The general methods of analysis are related to conventional vacuum technique, handling the gases at low pressures over

mercury and solid reagents. The gases are transferred by Toepler pumps, isolated by mercury cutoffs, and measured in a capillary pipet operating in a fashion analogous to a McLeod gage. The detailed apparatus and methods are an extension and refinement of those previously described by one of the authors (2).

Using this apparatus on a sample of from 1 to 25 cu. mm. at normal temperature and pressure, a general determination may be made for the components water, carbon dioxide, hydrogen, carbon monoxide, and oxygen or methane, the residual gas being taken as nitrogen. The errors vary from 5 per cent on the smaller samples to 2 per cent on the larger. We may define the error as the difference, between the amount of any one component and the value obtained for this amount by the authors' method of analysis, divided by the total amount of the sample. In a general analysis, the least detectable quantity of an individual component is about 0.06 cu. mm. In simpler analyses, such as on the carbon monoxide-carbon dioxide mixtures encountered in the filament studies, on account of the fewer manipulations required, it was possible to detect a quantity as small as 0.025 cu. mm., or about the amount of carbon monoxide in 1 sq. cm. of a monomolecular film.

This sensitivity has been obtained with intentional sacrifice of the accuracy obtainable with former variations of this type of equipment. On apparatus more similar to that previously described (2), with longer mercury columns and larger volumes of reagents, 0.5 per cent accuracy has been obtained on samples of 200 to 400 cu. mm.

### Apparatus

The apparatus is mounted on a rack 1.5 meters (5 feet) long and 2.2 meters (7 feet 4 inches) high as shown in Figure 1. The glassware, except where specified, is of Pyrex chemical glass throughout.



The detail of the capillary pipet is shown in Figure 2, A. This is a 1-mm. capillary 10 cm. long, on which is ground a series of graduations. In taking a measurement the mercury is raised to one of these graduations (by applying compressed air to the mercury reservoir) and the pressure read on the comparison manometer made from the same piece of capillary tubing. The pressure-volume product measures the quantity of gas. The mercury level, normally standing as shown in Figure 2, is drawn down to permit the gas to flow into the absorption train. The gas is circulated by operation of the Toepler pump (Figure 2, B), pumping the gas back into the pipet. The gas is collected by lowering the mercury column of the pipet to assume its normal level and continuing pumping as before.

This Toepler pump is actuated by compressed air and is arranged for automatic operation. Air from the laboratory high-pressure line is led through a reducing valve, measured by a gauge, and admitted to the mercury well of the pump by an electric solenoid valve. This is installed to operate as a two-way stopcock, connecting the mercury well first to the controlled pressure line and then to the atmosphere. Three electrical contacts sealed into the pump actuate a vacuum tube circuit (Figure 4) and a polarized telegraph relay which in turn operates the solenoid valve.

The particular design of the Toepler pump reduces the volume of mercury flowing past the cutoff which traps the gas forced over at each stroke of the pump. A simpler design (2) permitted some small bubbles of gas to escape by being trapped and swept out in the moving mercury column.

The same controlled air pressure offers a convenient means of adjusting the mercury in the pipet when measurements are taken. In fact, the most convenient, though not foolproof, method of handling all the pipets, Toepler pumps, etc., has been to pipe each mercury reservoir through a needle valve into a manifold to which could be connected at all the atmosphere, rough vacuum, or controlled pressure line, or the same pressure line in series with the solenoid valve.

To evacuate the system and admit gases, etc., the analysis apparatus proper, gas reservoir, and auxiliary equipment as well, are connected to a "header" which leads, through a large mercury cutoff (Figure 2, C), to the pumps. These, not shown, are a water-cooled mercury diffusion pump and a mechanical oil fore pump.

The absorption train consists of a series of reagent tubes, each of which is placed between a pair of mercury cutoffs (Figure 2, D). Each tube is by-passed by a third, so that by raising or lowering the proper cutoffs, the gas may be forced through the desired reagent or diverted around it. In order to keep the volume of the system as small as possible, the cutoffs were made approximately 2.5 cm. (1 inch) high of 0.6-cm. (0.25-inch) diameter tubing. To compensate for fluctuations in barometric pressure, small leveling bulbs are set in an adjustable platform 76 cm. below the absorption train. The bulbs have downward tubular extensions, and slide up and down on the vertical tube containing the mercury column as the cutoffs are raised or lowered, or the platform is adjusted by means of thumb screws.

The reagents used in the absorption train are copper oxide, magnesium perchlorate, and soda lime. The absorption tubes used for the magnesium perchlorate and soda lime follow the design shown in Figure 3, D. In each

tube about 0.3 gram of the reagent is retained between plugs of glass wool. For most of their work the authors have used a copper oxide tube of the same design. This was packed with Pyrex glass wool upon which was evaporated and decomposed a solution of about 1 gram of cupric nitrate. This produced a tube of relatively high flow resistance.

In the last evolution of the apparatus the authors have used a miniature mercury diffusion pump (Figure 3, F) to circulate the gases. This required a copper oxide tube of lower flow resistance which was constructed as shown in Figure 3, E. Cupric oxide, in wire form (0.8 gram), was powdered and placed in a transverse sandwich between layers of Pyrex wool and copper screen, retained by indentations in the wall of the glass tube. This was reduced and reoxidized before use. A similar construction was tried for the magnesium perchlorate and soda lime tubes, but the absorption was inefficient.

A platinum filament lamp (Figure 3, A) served as a slow-combustion pipet. This was mounted between cutoffs in the absorption train. The authors have used filaments of either c. p. platinum or the stronger alloy 80 per cent platinum, 20 per cent rhodium. Contrary to expectation, either filament is readily attacked by oxygen at 700° C., or above, to an extent sufficient to limit its use to the combustion of oxygen in an excess of hydrogen or carbon monoxide.

The water-cooled tube is constructed of Pyrex glass and the filament leads are very heavy platinum wire. The authors attempted to seal the platinum through the Pyrex glass using a silver burnishing paste. The seals were not quite tight and have been backed up with sealing wax. This procedure has so far caused no difficulty but is not to be recommended.

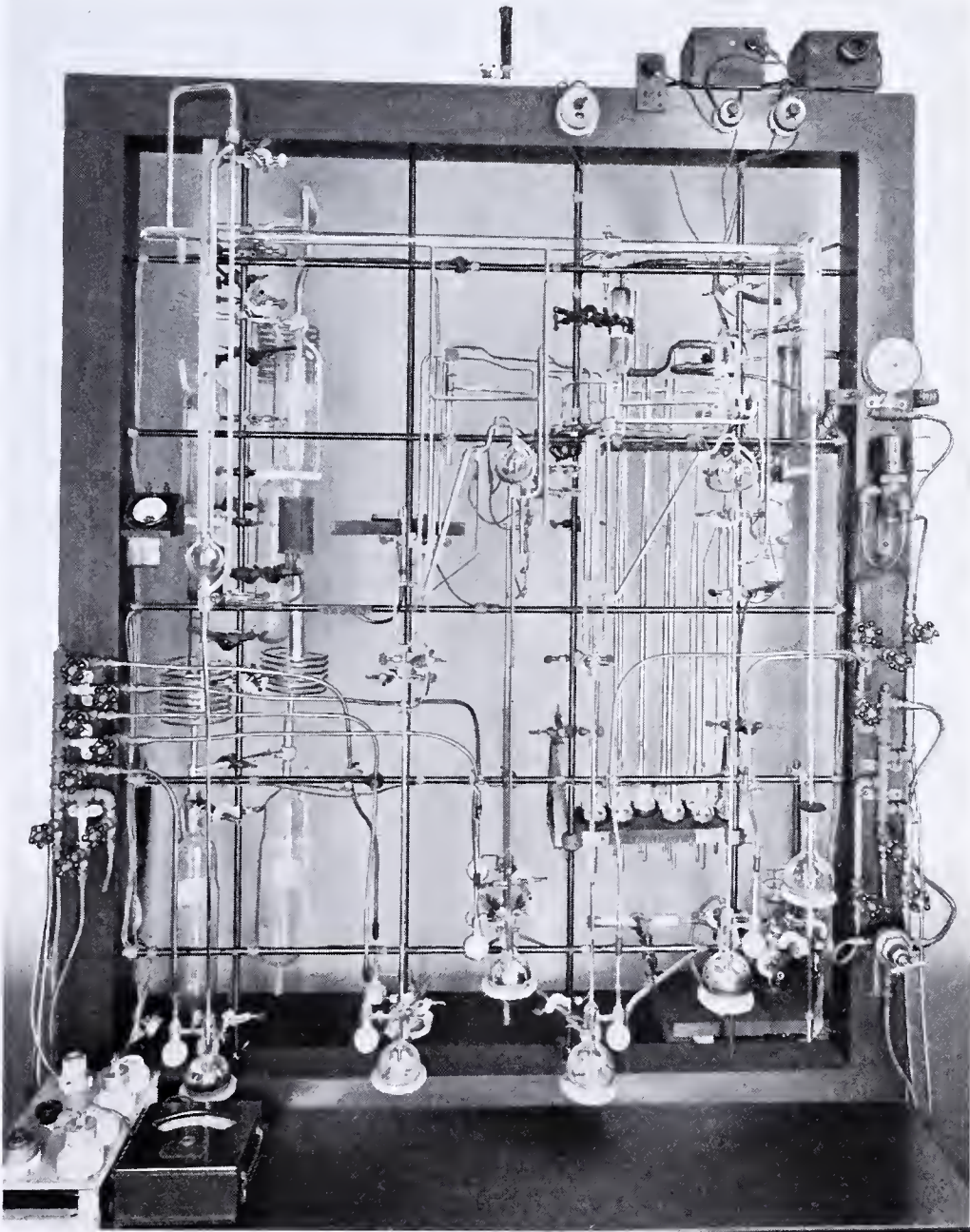


FIGURE 1. APPARATUS FOR ANALYSIS OF GAS



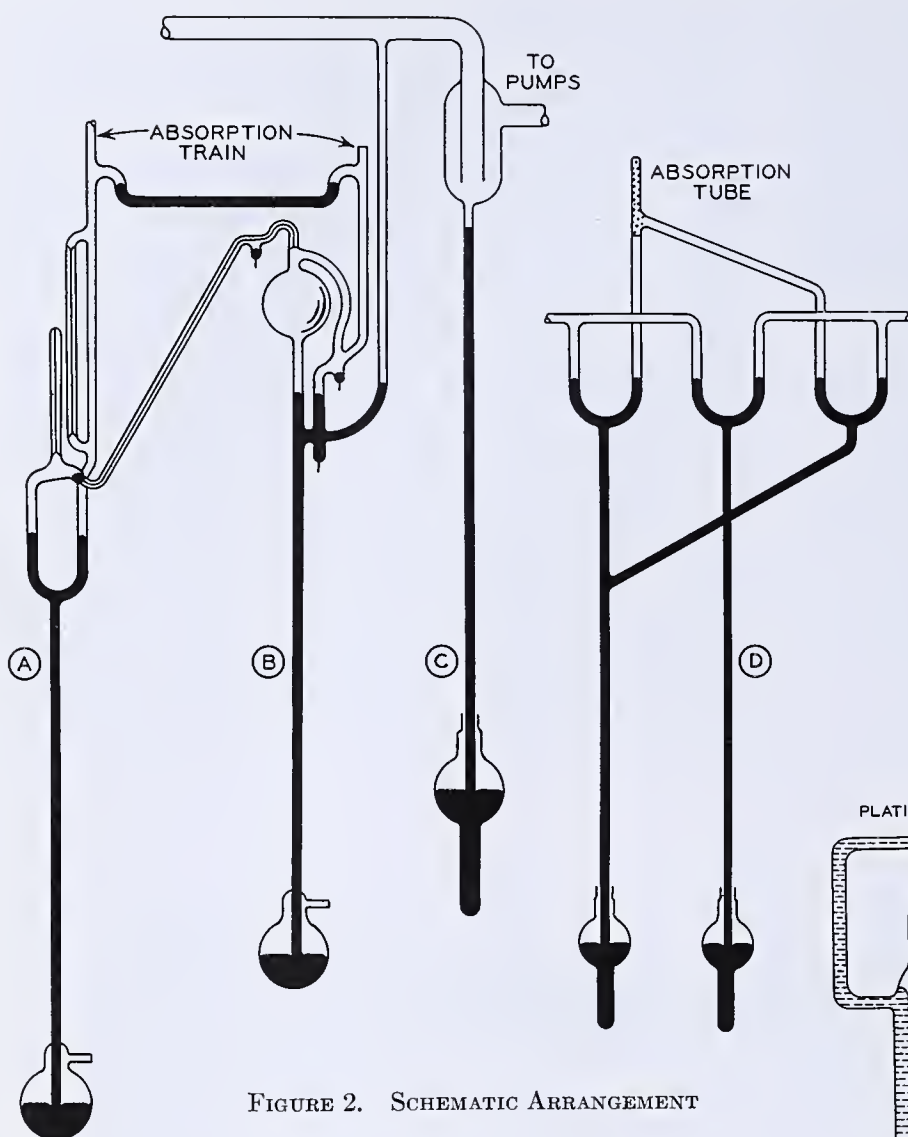


FIGURE 2. SCHEMATIC ARRANGEMENT

A method more in accord with standard practice would be to weld in a short section of tungsten which should be completely embedded in a bead of Corning g702p glass.

An explosion pipet is shown in detail in Figure 3, B. This is a small tube of soft lead glass, with barely exposed platinum leads, connected to its support by a graded seal. This pipet and a second Toepler pump are mounted the same as Figure 2, A and B. The inlet and exit tubes, however, are led to a reagent position in the absorption train.

One further element in the absorption train is a small liquid air trap similar in construction to the absorption tube shown in Figure 3, D (but without the constrictions to retain glass wool), mounted in an inverted position.

The gas reservoirs, made of soft glass, are shown in Figure 3, C. The method of admitting gas depends on the surface tension of mercury and the fact that porous plugs of baked Italian lavite may be sealed tightly to soft lead glass. One such plug is attached to the container and another to a flexible glass helix connected to the header, both being kept below the surface of a mercury reservoir. The plugs are too dense to permit the flow of mercury, but, on bringing the plugs into contact, gas flows through from the container into the header.

### Procedure

Prior to an analysis the reagent tubes must be thoroughly outgassed. The magnesium perchlorate and soda lime are baked at 250° C. for a half hour. The copper oxide is baked at 350° C. and then maintained at 300° C. during the analyses. The platinum filament is glowed at 1000° C. *in vacuo* previous to use. If the apparatus has been down to air, the filament is also conditioned for the removal of oxygen. A sample of hydrogen is circulated over the filament and through the magnesium perchlorate tube till there is no further reduction in quantity. When the filament was first installed a sample of carbon dioxide was circulated over the filament to burn out

traces of carbon. This filament is operated at a current corresponding to an observed temperature *in vacuo* of 720° C.

A sample of gas to be analyzed may be introduced into the header, or, if 100 per cent of the gas is to be collected, it should be evolved in apparatus associated with the absorption train. By operation of the Toepler pump (Figure 2, B) the sample is collected and measured in the capillary pipet (Figure 2, A).

The gas is then analyzed by circulation in turn through combinations of reagents in the absorption train. After each absorption the remaining gas is collected and measured. The amounts of water, carbon dioxide, hydrogen, carbon monoxide, nitrogen, and oxygen or methane may be computed from the progressive differences. The various steps follow in serial order.

1. Water vapor is first absorbed by circulation through the magnesium perchlorate.

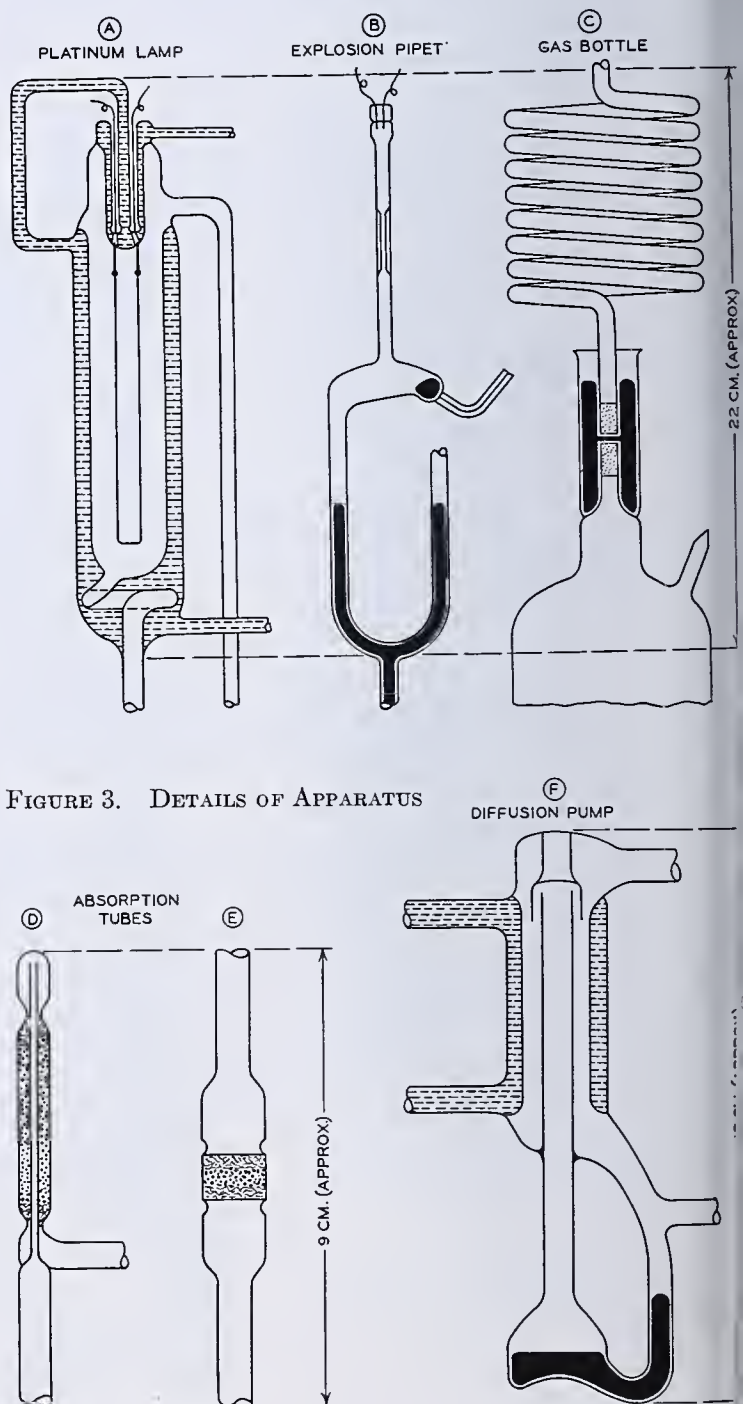


FIGURE 3. DETAILS OF APPARATUS



2. Carbon dioxide is next absorbed by circulation through the soda lime.  
3. If analysis be made for oxygen (with methane absent), the gas is next circulated through the platinum lamp and magnesium perchlorate in series. This removes oxygen and some hydrogen. There must be an excess of hydrogen plus carbon monoxide.  
4. Any carbon dioxide produced in step 3 is absorbed in the soda lime.  
5. Next hydrogen is absorbed by passing through the copper oxide and magnesium perchlorate in series. Carbon monoxide is also oxidized, but this involves no change in the amount of gas measured.  
6. Finally carbon monoxide is absorbed by circulation through the copper oxide and soda lime.  
The residue should be nitrogen. If methane be present the analysis cannot be made for oxygen, as the platinum lamp step would be indeterminate. Since methane is unaffected by the copper oxide, it will remain in the residue from step 6.  
7. To this residue is added 2.5 to 3 times as much oxygen. The gas is pumped into the explosion pipet, compressed to around 17 cm., and exploded by a spark from an induction coil. The gases are recovered and measured, first pumping through magnesium perchlorate and then direct circulation through copper oxide and magnesium perchlorate till absorption is complete removes any water or hydrogen. Excess oxygen is so removed, since the copper oxide tube contains reduced copper as well.  
8. Finally carbon monoxide, plus carbon dioxide, equivalent to the original methane, is removed by circulation through copper oxide and soda lime.

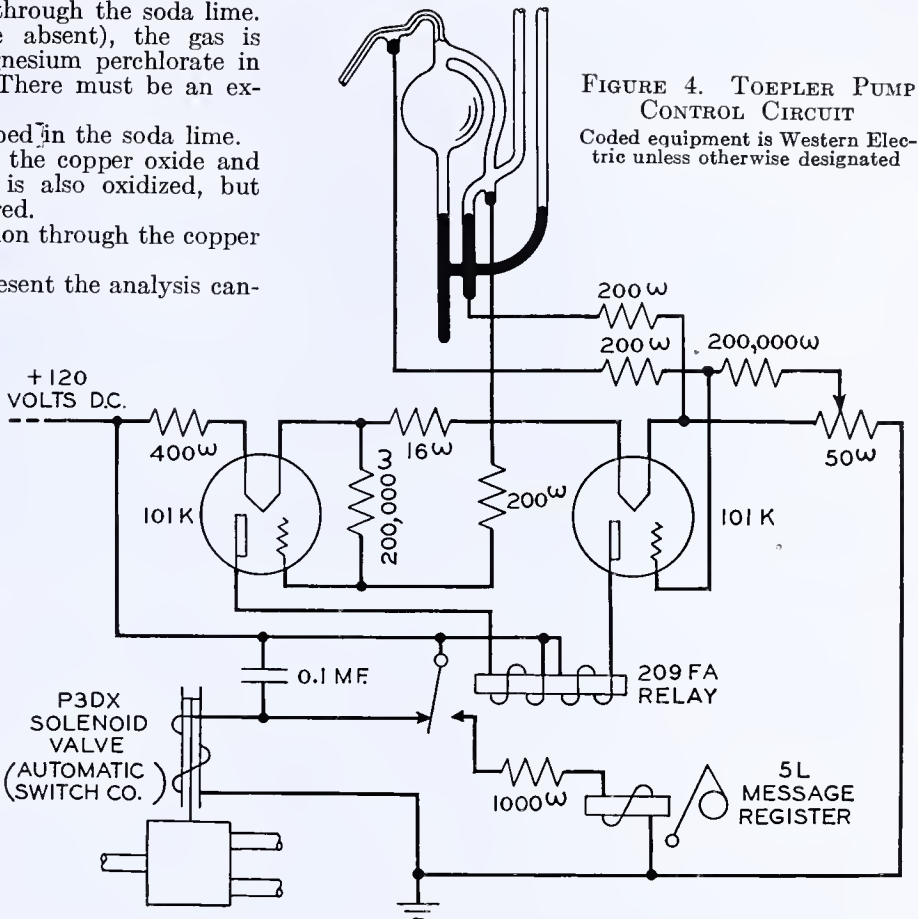
In most of the authors' work the gas has been circulated and recovered by the use of the Toepler pump. In general, twenty strokes of the pump each were adequate for circulation and collection. During collection the by-pass cutoff for each absorption tube was lowered to reduce the flow resistance. Each absorption was repeated till duplicate measurements were obtained. With a pump cycle of 25 seconds a duplicate circulation and collection required a minimum of 35 minutes. In view of other manipulations required and the fact that carbon monoxide absorption was usually slow, the time for a general analysis was to 6 hours.

TABLE I. ANALYSES OF SYNTHETIC MIXTURES

		Composition by Analysis			
		%	%	%	%
		Mixture 1			
Composition by Synthesis %		Initial Volume <sup>a</sup>			
		8.36 cu. mm.	22.4 cu. mm.	1.66 cu. mm.	1.83 cu. mm.
O <sub>2</sub>	36.9	35.7	35.4	32.1	31.9
	15.7	15.8	16.8	18.3	20.5
	13.0	11.9	13.8	14.9	13.5
	34.4	35.2	33.3	30.8	30.6
	..	1.4	0.7	3.9	3.5
		Mixture 2			
		Initial Volume			
		21.8 cu. mm.	6.34 cu. mm.	1.57 cu. mm.	0.946 cu. mm.
O <sub>2</sub>	22.3	22.4	21.2	22.8	21.8
	9.3	9.8	10.0	10.7	10.8
	35.5	35.8	36.5	32.7	32.9
H <sub>2</sub>	32.8	31.5	31.2	30.2	29.4
	..	0.5	1.1	3.6	5.1
		Mixture 3			
		Initial Volume			
		6.46 cu. mm.	11.14 cu. mm.	1.74 cu. mm.	0.598 cu. mm.
O <sub>2</sub>	31.8	31.0	30.5	29.8	38.3
	22.5	21.6	21.5	21.9	15.3
	8.1	8.1	8.0	9.8	7.0
	37.6	37.9	38.8	35.0	32.7
	..	1.4	1.2	3.5	6.7

<sup>a</sup> At normal temperature and pressure.

In the latest form of the apparatus the authors have incorporated a miniature diffusion pump (Figure 3, F) close to the receiver of the Toepler pump. This is similar to a design shown by Norton and Marshall (1). This pump is mounted between cutoffs and with a by-pass so the equipment can be



operated as before. Another cutoff connects with the front of the absorption train, so that the diffusion pump can be used either to circulate the gas or to pass it into the Toepler pump. With this arrangement, and the new copper oxide tube (Figure 3, E), 2 minutes are sufficient for circulation, and four strokes of the Toepler pump for collection. This permits a duplicate circulation and collection in 8 minutes. Since the absorptions are usually complete and a third circulation is rarely required, the total time of a general analysis has been reduced to one hour. There is no reaction between hot mercury vapor and any of the gases considered.

Analytical Results

As examples of the results obtainable with this apparatus, analyses upon three synthetic mixtures are included. The samples range from 0.6 to 25 cu. mm. at 0° C. and one atmosphere. The original proportions were determined by measuring each gas in the calibrated pipet. The analyses of these mixtures indicate errors ranging from 2 per cent on the larger samples to 5 per cent on the smaller, the smallest sample showing errors of 7 per cent.

These results are shown in Table I. Mixtures 1 and 2 were analyzed using the Toepler pump technique, while mixture 3 was manipulated using the miniature diffusion pump.

The errors seem due to the adsorption and desorption of gases on the apparatus, particularly the powdered reagents, and therefore increase progressively with decreasing size of the sample. This is evidenced by the appearance of nitrogen which is absent from the synthetic mixtures. Correction could be made for this systematic error in nitrogen, but this has seemed hardly justified, since other errors are of the same order of magnitude.

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(1) Norton and Marshall, General Electric Co. Reprint 613: (abstract), *Am. Inst. Mining Met. Engrs.*, 102, 287 (1932); 104, 136 (1933).  
(2) Prescott, C. H., Jr., *J. Am. Chem. Soc.*, 50, 3237 (1928).  
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## CHEMICAL ENGINEERING BUILDING AT THE VIRGINIA POLYTECHNIC INSTITUTE

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**T**HE new chemical engineering building at the Virginia Polytechnic Institute opened for undergraduate and graduate instruction at the beginning of the fall quarter of the 1938-39 session. The new structure, with exterior wall of local blue limestone, adjoins the present geology, physics, and chemistry building, known as Davidson Hall, conforming in architecture and construction.

The size, shape, and interior arrangement are shown in the floor plans. The building is rectangular, with one section three stories high, and the other with a headhouse or room extending open to the same level as the three-story section. The building provides 11,416 square feet of laboratory, office, classroom, storage, and library area. The over-all dimensions are  $171 \times 35 \times 31$  feet, and cost \$76,000 or 41 cents per cubic foot. This includes plumbing, heating, ventilating, and electrical work, and process piping. The present installed equipment value approximates \$31,000.

The interior of the building is of 3-inch cinder block and concrete, with some rooms finished with cement-sand plaster, followed with three coats of paint. The cinder block provides an inexpensive acoustic material for the walls. The floors are of reinforced concrete, surface-treated to prevent dusting.

### Unit Operations Laboratory

This laboratory, in which permanent equipment is erected, has a ground floor area of 2330 square feet and a balcony area of 400 square feet. The ground floor is provided with concrete floors 6 inches thick and three lines of floor drains running the length of the laboratory; the drains are covered with removable cast-iron grid covers  $1 \times 2$  feet; the floors slope to the drains with a pitch of 1 inch in 8 feet. The open area, extending up to the 31-foot level, is approximately 32 feet wide and 56 feet long, with a rolling bridge on a track at the 25-foot level. This bridge is constructed to support a 5-ton load, a beam-trolley permitting attachment of hoists; the flooring on the bridge makes it also a work area. On the walls inserts are placed on 4-foot centers for attachment of equipment and intermediate supports. There are no windows on the lower portion of the side and end walls, the lower edge of the first level of windows being at the 12-foot level. The upper bank of windows is on the balcony level.

Service provided in this area consists of high- and low-pressure steam, hot and cold water, high- and low-pressure air gas, and power lines. The process lines run at the 17-foot level underneath the balcony and service the equipment from that level; all piping service is overhead in this area.

A section of this laboratory is enclosed for grinding equipment. A dust collector and a fume fan provide clean air for the grinding room; this provides for 35 air changes per hour. The crushing and grinding equipment housed in the grinding room consists of a ball mill, a hammer mill, a disk mill, a jaw crusher, a standard shaking machine, and a Williams roller mill with complete dust-separation equipment.

Around the remainder of the laboratory are located the following:

Filter area with 18-inch Sperry plate and frame press, a 24-inch stoneware vacuum filter, a 500-, 100-, and 42-gallon sedimentation system, a Feine continuous filter, and a 6-foot Dorr double-tray thickener; still and 15-plate fractionating column; batch vacuum still; Pyrex heat exchanger with fluid flow assembly combined triple-effect evaporator with one 24-inch diameter vertical-tube effect, one 88-tube horizontal-tube effect, and one 10-long forced circulation-tube effect, the system capable of running under any modifications of feeds and order of effects; absorption tower assembly of stoneware, 24 feet high, 18 inches in diameter; drying area with a 12-tray atmospheric dryer, a Buflovac vacuum double drum dryer, a 4-tray vacuum shelf dryer, and an experimental air-conditioned dryer; centrifugal area with a 26-inch basket centrifugal and a high-speed supercentrifuge; vacuum impregnator; water softener; 3 small open kettles of copper and cast iron mixing kettles; two electric furnaces; two Hytor compressors crystallization pans; and three-roll compounding mill.

The balcony is provided with steep sloped floors and drains curbing, and subway grating sections which may be removed so that equipment may be erected up through the balcony floor.

Two small blast heaters on the balcony and one large unit on the lower floor provide for movement of air and heating. Two powered ventilators in the roof assist in the removal of air from the laboratory. These units provide for 35 changes of air per hour.

### Development and Projects Laboratory

The development and projects laboratory occupies 130 square feet of the other end of the ground floor from the main



unit operations laboratory, at the same level and with the same drainage and floor construction. The height of this area is 10 feet with inserts in the ceilings and side walls at 4-foot centers. No permanent equipment setups are provided for this area. Senior research problems and development laboratory studies use this laboratory for the temporary assemblies; movable heavy oak laboratory tables,  $8 \times 3 \times 3$  feet, are available. Three fume ducts assist in carrying away confined fumes through flues to the roof. Heating and ventilation of this laboratory are accomplished by means of an automatic blast heater connected with outside air at the end of the laboratory, carrying heat and air through the laboratory, through the center piping areas, thence into the main laboratory. This unit can be operated to provide 35 changes of air per hour.

### Miscellaneous

**GRADUATE RESEARCH ROOMS.** Four research laboratories are provided on the second floor, above the development laboratory; these are approximately  $10 \times 23$  feet in dimensions, provided with sinks, tables, desks, and floor drains. These provide for eleven men. Additional space for increased enrollment of graduate students is available in the connected section of adjoining Davidson Hall.

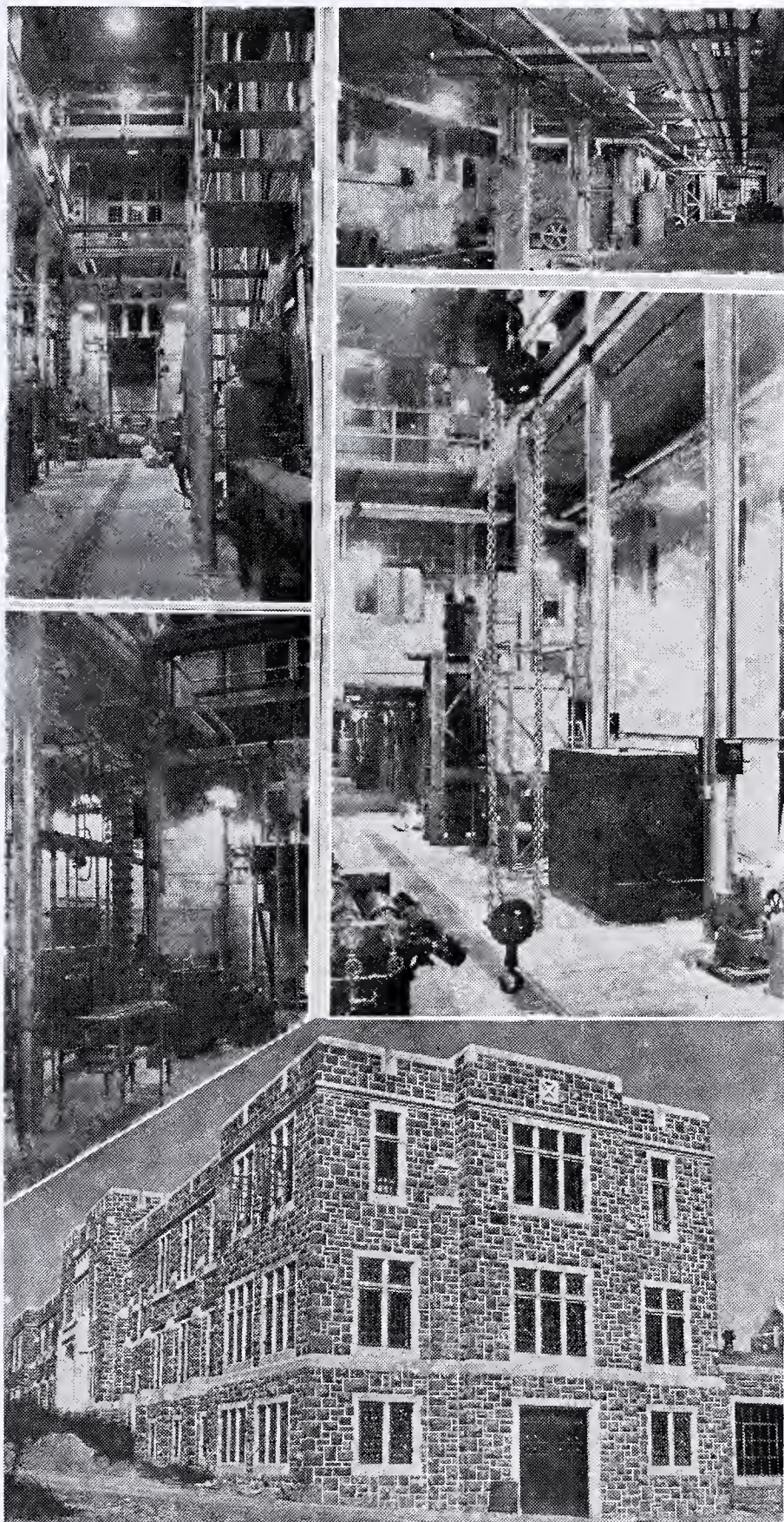
**WORKSHOP AND PIPING AREA.** The workshop and piping area are located on the ground floor, occupying a portion of the center section. A lathe, tool grinders, drill press, and appropriate tool cases are located here. In the piping area a rack holds various sizes of pipes. Here are also located a pipe work-bench with two pipe vises and a machine-bench with machine vises. A separate room for all fittings is located in this area.

**STORAGE AND INSTRUMENT ROOMS.** The chemical storage is located on the ground floor in the central section and provides  $10 \times 14$  feet of floor space. A flue keeps the air fresh. The instrument room is located next to the chemical stores and opens upon

the main laboratory. A second instrument room is provided on the second floor.

**OFFICES.** The main office is located on the second floor, near the main entrance, and overlooks the main unit operations laboratory; the three smaller offices are located on the third floor, readily accessible to the classrooms and the balcony.

**CLASSROOMS.** The main classroom is located on the second floor and has a capacity of sixty students. The small classroom is located in the center of the third floor and



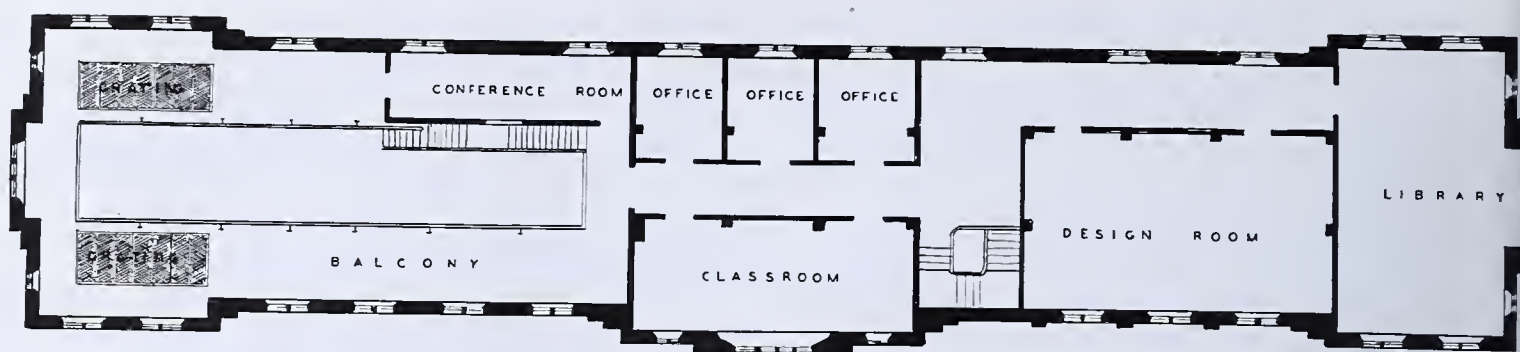
Upper left and left center. VIEWS OF UNIT OPERATIONS LABORATORY

Upper right. SENIOR PROJECTS AREA

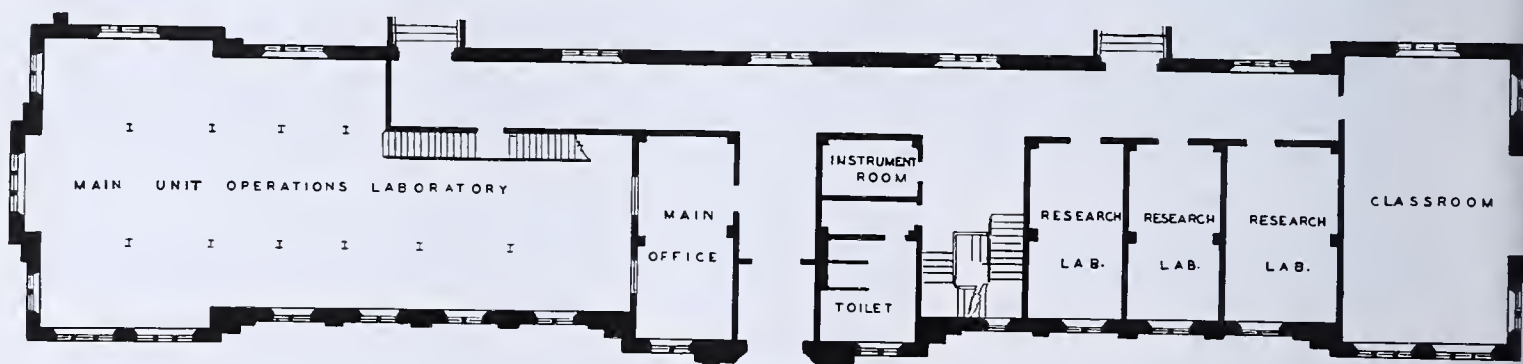
Right center. UNIT OPERATIONS LABORATORY, WITH CRANE IN FOREGROUND

Bottom. EXTERIOR, FACED WITH NATIVE Limestone AND TRIMMED IN WHITE ARTIFICIAL STONE



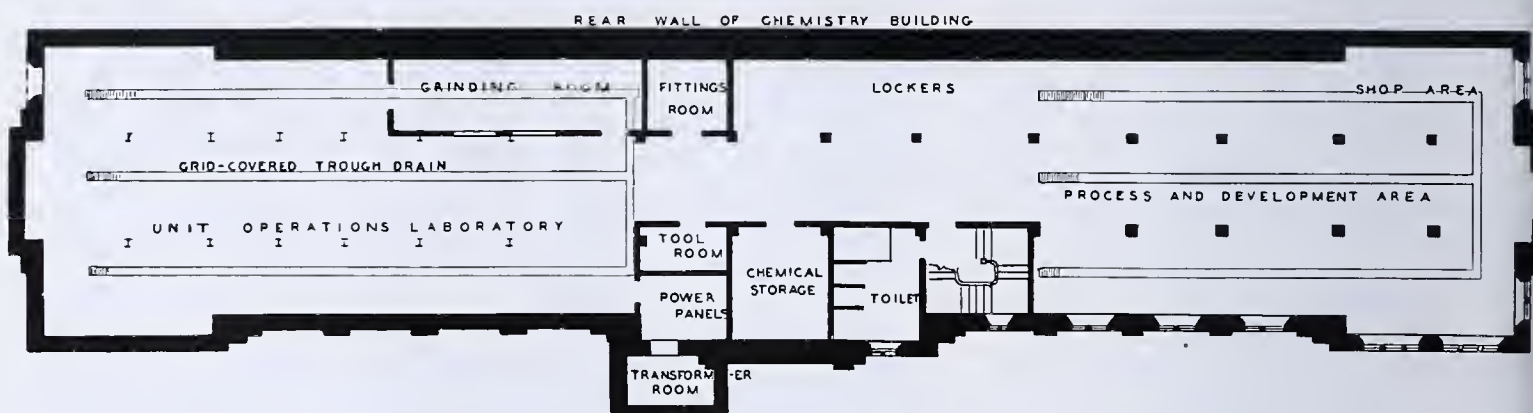


SECOND FLOOR PLAN



SCALE: 1/8" = 1'

FIRST FLOOR PLAN



GROUND FLOOR PLAN

accommodates thirty students. The design room is fitted with twenty desks for design, the class being conducted on a section basis; this room also serves as a classroom. The conference room is located over the corridor and accommodates from four to eight men.

Heating of small rooms and classrooms is carried out by low-pressure steam radiators. Corkboard bulletin boards are provided on each floor; blackboards in all classrooms; and hat and coat racks on each floor.

**LIBRARY AND STUDY HALL.** The library is located on the third floor and is the same size as the large classroom which is located directly underneath it. It is provided with six cases with 30 feet of books each. Four study tables, 8 feet long and 3 feet wide, provide the facilities for reading and study and also serve for conferences. A 24 drop-leaf compartment periodical case with current issues is also provided.

**ELECTRICAL SERVICE.** Electrical service for the building is taken from the campus underground system into the transformer room, at 2300 volts, 3-phase, 60-cycle. Three 75-kva. transformers are connected in delta in the primary side and star connected on the secondary to give a 4-wire, solid neutral service with 208-volt single-phase, 208-volt 3-phase, or 120-volt single-phase from any phase to ground. The Bussway system of power lines is used to distribute the service to

all parts of the laboratories. Boxes are provided at 16-foot intervals to permit additional servicing; at present 3-wire 120-volt plugs are placed at 4-foot intervals and safety switches for from 3 to 10 horsepower at 8-foot intervals on laboratory walls and columns. Each set of four 208-volt safety switches and each set of eight 120-volt 3-way plugs are provided with dead-front "no fuse" circuit breakers. All equipment and the plugs are grounded through a ground wire in the system. The general lighting system is provided on a separate system; solaire light fixtures are provided in the offices, classrooms, and library, and dome fixtures in the laboratories.

**PROCESS PIPING.** The process piping, consisting of 60-pound, 15-pound, and 1-pound-gage steam, hot and cold water, air, and gas are installed in the overhead all-exposed manner. Service cocks and valves are provided at 8-foot intervals in all working areas. In the large laboratory the piping for each piece of equipment is taken off the central balcony lines down to the equipment, eliminating any cross lines over the working areas. The main supply lines are as follows: 1.5-inch for 60-pound, 3-inch for 15-pound, and 4-inch for 1-pound-gage steam pipe; 2-inch soldered-fitted copper water pipe, hot and cold; 1.25-inch gas and air black iron pipe. All fittings on the water lines are stream-lined soldered.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Iodine in Sodium Tetraiodophenolphthalein

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The iodine assay of sodium tetraiodophenolphthalein was studied with the object of producing a method which (1) would ensure a complete decomposition of the organic matter in the sample, (2) would give an accurate determination of the iodine, and (3) would be rapid and suitable for a routine procedure.

In the permanganate-silver nitrate method which was developed, the organic matter is completely destroyed by means of alkaline permanganate and the iodide is accurately determined argentimetrically using an adsorption indicator. The process is simple and rapid, a complete analysis requiring about 1.5 hours.

THE method for the determination of iodine in sodium tetraiodophenolphthalein (soluble iodophthalein, U. S. P. I) described in this paper is based upon a study of various existing methods, supplemented by certain new features made possible through recent developments in analytical chemistry. In brief, a method is proposed in which the organic matter in the sodium tetraiodophenolphthalein is decomposed with alkaline potassium permanganate, and after acidification the excess permanganate is reduced with sodium bisulfite. The iodide is titrated with silver nitrate and the end point is detected by means of an adsorption indicator such as diiodo-rescein.

The quantitative determination of iodine contained in organic compounds has received considerable attention in recent years, and its determination in sodium tetraiodophenolphthalein has been described by several investigators. Delbridge (4) proposed a method in which the sample was subjected to a combustion with lime, and after acidification was titrated with silver nitrate and thiocyanate according to the Volhard (12) method. Seeker and Mathewson (11) described a method in which the organic matter was destroyed with acid potassium permanganate, the excess permanganate was reduced with sulfur dioxide, and the iodide was precipitated and weighed as silver halide.

Leclercq (7) recently reviewed the determination of iodine in organic compounds and included a study of the methods for iodine in sodium tetraiodophenolphthalein (8). He compared, among others, a so-called "international method" with the classical methods of Carius (3) and Baubigny and Chavanne (2), and with the official U. S. P. XI method. As a result of his study, Leclercq favored the international method as most practical and effective for sodium tetraiodophenolphthalein. In the international method, the sample is intimately mixed with an alkaline oxidizing mixture consisting of potassium carbonate, sodium carbonate, and potassium nitrate. The mass is heated to fusion in a nickel crucible, the melt is extracted with hot water, and the solution is treated with sodium hypochlorite to ensure complete conversion of the iodine to iodate. Excess chlorine is removed by boiling, the solution is neutralized, and after addition

of potassium iodide the liberated iodine is titrated with thiosulfate. Leclercq also described a method in which an alkaline permanganate oxidation of the sample was followed by treatment with alcohol, and after addition of potassium iodide the liberated iodine was titrated with thiosulfate.

The official method for sodium tetraiodophenolphthalein (9) consists essentially in a fusion of the sample (as tetraiodophenolphthalein) with sodium carbonate, followed by extraction and acidification of the residue and subsequent titration with potassium iodate according to the method of Andrews (1). This is not a rapid method, and furthermore it is subject to several inherent errors which combine to give a low value for iodine. Free iodine is lost by volatilization and the sodium tetraiodophenolphthalein is not completely decomposed during the sodium carbonate fusion. The iodine lost during the fusion process was found to amount to as much as 1 per cent of the weight of the sample. The iodine left in the mass in the form of undecomposed sample varied in quantity, probably depending on the temperature and length of time of the fusion. This iodine was found to amount to about 3 per cent.

In order to establish the fact that free iodine is lost during the fusion process in the U. S. P. XI method, and that the fusion mass contains undecomposed material, the following experiments were carried out:

A large porcelain crucible was inverted over the crucible covering the fusion mixture, but an air space of several millimeters was allowed between the crucibles. A porcelain tube was sealed to the upper crucible through a hole bored in the bottom. This tube was in turn attached to a Pyrex glass tube leading into a bulb which could be chilled in ice. Fusion was carried out in the regular manner over a Bunsen flame with the crucible heated to a dull red. During the fusion a very slow stream of air (one to two bubbles per second) was aspirated through the system leading to the chilled tube and the free iodine lost from the fusion mass



was collected in this tube. At the conclusion of the fusion process the Pyrex tube was removed and washed with a solution of potassium iodide. The solution containing the iodine was then titrated with sodium thiosulfate and the value for the recovered iodine calculated.

The experiment was completed by the regular U. S. P. XI procedure and the percentage of iodine in the sample calculated. In addition, that portion of the fusion mass which was insoluble in the extraction process, and thus collected on the filter paper during the filtration, was analyzed for iodine according to the permanganate-silver nitrate method described in detail below.

TABLE I. SODIUM TETRAIODOPHENOLPHTHALEIN SAMPLE A-1

	Iodine %
Found in tetraiodophenolphthalein by U. S. P. XI method	56.33
Recovered (volatilized during fusion)	0.75
Recovered from fusion residue	3.27
Total iodine found	60.35
Same sample by proposed method	60.59

It was shown by these experiments that iodine was lost during the fusion process, and that the U. S. P. XI fusion procedure does not completely decompose the sample. The experiments were carried out on a single sample of tetraiodophenolphthalein precipitated and separated according to the U. S. P. XI method, and then divided into two parts. One portion was treated by the regular U. S. P. procedure; the other portion was analyzed by the permanganate-silver nitrate method described in this paper. The results given in Table I show that the iodine found by the U. S. P. XI method when added to the iodine volatilized during fusion and to the undecomposed iodine gave a total iodine very nearly the same as the quantity found by direct analysis of the second portion by the proposed permanganate-silver nitrate method.

TABLE II. DETERMINATION OF IODINE IN SODIUM TETRAIODOPHENOLPHTHALEIN

Sample	I by $\text{KMnO}_4$ - $\text{AgNO}_3$ %	I by $\text{KMnO}_4$ - $\text{KIO}_3$ %	Sample	I by $\text{KMnO}_4$ - $\text{AgNO}_3$ %	I by $\text{KMnO}_4$ - $\text{KIO}_3$ %
A-2	...	53.42	B-1	...	54.31
A-3	53.70 <sup>a</sup>	...	B-2	54.21 <sup>a</sup>	...
A-4	53.78 <sup>a</sup>	...	B-3	54.51 <sup>b</sup>	...
A-5	53.51 <sup>a</sup>	...	B-4	54.40 <sup>a</sup>	...
A-6	53.54 <sup>b</sup>	...	B-5	54.48 <sup>b</sup>	...
A-7	53.66 <sup>b</sup>	...	B-6	54.33 <sup>b</sup>	...
A-8	53.66 <sup>b</sup>	...	B-7	54.50 <sup>a</sup>	...
Av. 53.64			B-8	54.30 <sup>b,c</sup>	...
			Av. 54.39		

<sup>a</sup> Eosin indicator.

<sup>b</sup> Diiodofluorescein indicator.

<sup>c</sup> 5% chlorine, as sodium chloride, was added to this sample before making the analysis.

Five analyses by the U. S. P. XI method gave results all more than 3 per cent lower than the values obtained by the permanganate-silver nitrate method, and, furthermore, the five analyses varied between themselves by as much as 3 per cent (Table II).

### Preliminary Development of Method

An attempt was made to develop a procedure which would give more reliable results than the U. S. P. XI method, and at the same time would be more rapid and suitable for routine analysis. Before this was fully developed, the permanganate-iodate method was tested. An alkaline solution of the sodium tetraiodophenolphthalein sample was treated with a saturated solution of potassium permanganate, the solution was acidified, and the excess permanganate was reduced with sulfurous acid. An adjustment was made with 0.02 N potassium permanganate to the point where the clear solution showed the first trace of yellow color. The solution was made strongly acid with hydrochloric acid and the titration was carried out with potassium iodate as in the U. S. P. XI method.

This procedure gave fairly consistent results, considerably higher than by the U. S. P., but, as shown in Tables II and III, slightly lower than the values obtained by the perman-

ganate-silver nitrate method. The method was rapid and was used successfully in the authors' analytical laboratory for more than a year, but had certain features which were not altogether satisfactory.

The alkaline permanganate treatment was found very convenient for the destruction of organic matter in the sample, and more satisfactory than the various dry methods now in use. Leclercq (?) suggested the use of solid alkaline permanganate. His procedure also called for boiling the alkaline permanganate solution, and he reported that this caused a loss of iodine. The authors found that the oxidation was complete and no appreciable iodine was lost when an excess of a saturated solution of permanganate was added to a solution of the sample, and the resulting solution was digested on a steam bath for about 45 minutes.

TABLE III. DETERMINATION OF TETRAIODOPHENOLPHTHALEIN AND IODINE IN TETRAIODOPHENOLPHTHALEIN

Sample	Tetraiodo- phenol- phthalein by U. S. P. %	Iodine in By U. S. P. XI %	Iodine in Tetraiodophenolphthalein By $\text{KMnO}_4$ - $\text{AgNO}_3$ %	By $\text{KMnO}_4$ - $\text{KIO}_3$ %
A-1	...	56.33 <sup>a,b</sup>	60.59 <sup>b,c</sup>	...
A-9	86.35	53.94	...	...
A-10	86.32	57.12	...	...
A-11	86.21	56.52	...	...
A-12	85.75	...	...	...
A-13	...	...	...	60.24
A-14	...	...	...	60.13
A-15	86.23	55.43 <sup>d</sup>	60.56 <sup>e</sup>	60.45
A-16	86.95	...	60.50 <sup>e</sup>	...
Av. 86.30		55.87	60.55	60.29

<sup>a</sup> Loss of iodine during fusion determined as 0.75%.

<sup>b</sup> Reported in Table I.

<sup>c</sup> Diiodofluorescein used as indicator.

<sup>d</sup> Loss of iodine during fusion determined as 0.68%.

<sup>e</sup> Eosin used as indicator.

The Andrews iodate titration (1) offers an accurate end point but is not particularly satisfactory for a routine analysis because the operations of shaking and subsequent waiting for equilibrium are time-consuming. There is also a safety hazard involved, in that the flask nearly filled with concentrated acid must be shaken vigorously. For these reasons a method involving a direct titration appeared to offer distinct advantages. Fajans and Wolff (5) suggested the use of an adsorption indicator in the silver nitrate titration of iodide, and Kolthoff (6) recommended eosin and diiodofluorescein as indicators for titration of iodine in the presence of chlorine. It was found possible to make use of this titration in the determination of iodine in sodium tetraiodophenolphthalein. After the oxidation of the sample with alkaline permanganate, the excess permanganate was reduced with sodium bisulfite in place of the sulfurous acid used in the permanganate-iodate method, and either eosin or diiodofluorescein was found to be a suitable indicator. However, diiodofluorescein is recommended, since it produced a sharper end point in this particular case.

### Procedure for Permanganate-Silver Nitrate Method

Weigh accurately approximately 0.2 gram of sodium tetraiodophenolphthalein or tetraiodophenolphthalein into a 500-ml. Erlenmeyer flask and add 15 ml. of 5 per cent sodium hydroxide solution. Place the flask on a steam bath, and when the sample is completely dissolved, add 25 ml. of a saturated solution of potassium permanganate. Wash down the sides of the flask and let the solution digest on a steam bath for about 45 minutes, swirling the solution in the flask at about 5- or 10-minute intervals. Remove the flask from the steam bath, cool under the tap to room temperature, and add 75 ml. of distilled water and 1 ml. of dilute sulfuric acid. Add slowly from a buret a concentrated solution of sodium bisulfite until the solution in the flask becomes colorless. Finally add 2 ml. of glacial acetic acid, one 1.25-cm. (0.5-inch) cube of ammonium carbonate, and 1 ml. of a 0.5 per cent solution (in 70 per cent ethyl alcohol) of diiodofluorescein indicator. Titrate the solution in diffuse light with



0.1 *N* silver nitrate until the color changes from a brownish red to a bluish red color. [In case eosin indicator is used, add 20 drops of a 0.1 per cent solution (in 70 per cent ethyl alcohol) of the dye and titrate to the appearance of a pink color.] The results obtained by this method on two different samples of sodium tetraiodophenolphthalein are shown in Table II.

In the U. S. P. XI procedure for sodium tetraiodophenolphthalein, the iodine determination is carried out on the precipitated and dried tetraiodophenolphthalein. In Table II is shown a series of comparative analyses on the tetraiodophenolphthalein produced from portions of sodium tetraiodophenolphthalein sample A. The quantity of tetraiodophenolphthalein found in several analyses has also been tabulated. In analysis A-15, comparative results for iodine by three methods based on an identical sample of tetraiodophenolphthalein are shown.

Check by Pregl Combustion Micromethod

The Pregl (10) combustion micromethod was utilized as a check on the results obtained by the permanganate-silver nitrate method. The Pregl method was applied on a semimicro scale, and the iodine was determined both by weighing silver halide and titrating with silver nitrate using an adsorption indicator. The double microanalysis served as a check on both the iodide content of the sample and the titration method itself. If there was an appreciable quantity of chloride in the sample, the gravimetric method alone would be inadequate, but the titration method should not be influenced by the presence of chloride.

TABLE IV. IODINE IN SODIUM TETRAIODOPHENOLPHTHALEIN BY MICROMETHODS

Sample	Wt. of Sample Mg.	Wt. of Ppt. or Vol. of AgNO <sub>3</sub> Mg.	I by Gravimetric %	I by Volumetric %
A-17	31.01	23.22	53.82	...
A-18	20.02	14.62	53.88	...
A-19	18.15	13.27	53.80	...
A-20	30.21	21.76	53.82	...
Ml.				
A-21	28.10	1.192	...	53.84 <sup>a</sup>
A-22	30.82	1.308	...	53.86 <sup>b</sup>
A-23	20.77	0.882	...	53.89 <sup>a</sup>
Mg.			Av. 53.83	53.86
B-9	8.92	6.49	54.36	...
B-10	20.78	15.23	54.41	...
B-11	13.21	9.61	54.38	...
Ml.				
B-12	64.14	2.750	...	54.42 <sup>a</sup>
B-13	26.83	1.151	...	54.44 <sup>a</sup>
B-14	20.37	0.875	...	54.51 <sup>b</sup>
B-15	23.28	1.000	...	54.51 <sup>b</sup>
			Av. 54.38	54.47

<sup>a</sup> Eosin indicator.  
<sup>b</sup> Diiodofluorescein indicator.

Samples for the microanalyses were weighed on an assay balance sensitive to 0.01 mg., and the titrations were made with a microburet graduated to 0.02 ml. About 25 mg. of sodium tetraiodophenolphthalein were weighed into a platinum boat of about 3 × 4 × 12 mm. The boat with sample was introduced into a combustion tube constructed according to Pregl, and containing a glass spiral for the absorbent. The sample was burned in a slow stream of oxygen and the liberated iodine was absorbed in a saturated solution of sodium carbonate containing a few drops of sodium bisulfite solution. Oxygen was passed through the tube for about 30 minutes after the combustion was completed. When the tube was cool it was rinsed out with water. The excess of reducing agent was removed from the solution by the addition of a few drops of 27 per cent hydrogen peroxide. A mixture of silver nitrate and nitric acid was used to precipitate the silver halide and the precipitate was filtered on a platinum crucible having a very fine, dense platinum-sponge mat. The crucible and precipitate were dried in an oven at 250° C., cooled, and weighed as silver iodide. All details were carried out according to Pregl except in the use of the platinum-sponge crucible. The procedure for the volumetric micromethod was carried out exactly as in the gravimetric micromethod up to the point where the combustion process was completed. The combustion

tube was rinsed out, and the solution was made acid with acetic acid and titrated with 0.1 *N* silver nitrate using an adsorption indicator. Both diiodofluorescein and eosin were used in these analyses. The results by microanalysis are shown in Table IV.

TABLE V. COMPARISON OF AVERAGE RESULTS

	Iodine Found Sample A %	Sample B %
Semimicromethod	53.84 ± 0.03	54.43 ± 0.05
KMnO <sub>4</sub> -AgNO <sub>3</sub> method	53.64 ± 0.08	54.39 ± 0.09

The two micromethods gave fairly consistent results and agreed reasonably well with each other. The results obtained by the micromethods were slightly higher than, but still in close agreement with, the results by the permanganate-silver nitrate method (Table V).

Discussion

The permanganate-silver nitrate method is suitable for routine analysis of sodium tetraiodophenolphthalein. The sample is weighed directly into the flask and oxidation and titration are carried out in the same flask with no transfers involved. If the sample has not been completely decomposed by the permanganate treatment, this fact can easily be observed by the appearance of the solution after the excess permanganate has been reduced. The silver nitrate titration is rapid and the end point is easily detected. A single analysis can be carried out in about 1.5 hours, and it is possible to complete ten or more analyses in one day.

The U. S. P. XI procedure for sodium tetraiodophenolphthalein calls for the determination of tetraiodophenolphthalein, followed by an iodine assay on the dried sample of tetraiodophenolphthalein. The results of this determination are not particularly concordant, as can be seen by Table III. If the sample of sodium tetraiodophenolphthalein contains soluble iodide, it will not be detected by the present U. S. P. XI procedure. The control analysis of sodium tetraiodophenolphthalein could be very satisfactorily effected by means of an iodine determination on the original sample, supplemented by a test for soluble iodide. This procedure would eliminate the present unreliable and time-consuming determination of tetraiodophenolphthalein. The soluble iodide could be determined by dissolving a sample in water, precipitating the tetraiodophenolphthalein with acetic acid, and filtering. The filtrate and washings could be titrated with 0.1 *N* silver nitrate using diiodofluorescein as indicator. The end point with this indicator is sharp and reliable for small quantities of iodide in the presence of as much as 5 per cent of chloride. Samples A and B showed 0.29 and 0.26 per cent of titratable iodide, respectively.

Acknowledgment

The authors wish to express their appreciation to H. V. Farr and Melvin A. Thorpe for their cooperation and interest in this sodium tetraiodophenolphthalein assay investigation.

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# Determination of Dissolved Oxygen in Aqueous Solutions

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THE Winkler method is recognized as reliable except where very small quantities of dissolved oxygen are involved. Three types of errors may arise when applying this method to the estimation of traces of dissolved oxygen in water: (1) Impurities in the water such as nitrites, sulfites, iron ions, and organic matter may cause inaccuracies; (2) the correction for the dissolved oxygen added in the reagents may introduce uncertainties; (3) the dependence of the titration end point of the iodine upon the nature of the starch and upon the temperature introduces other uncertainties.

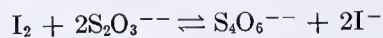
Theriault (8) has discussed the determination of dissolved oxygen by the Winkler method; an excellent bibliography on the determination of dissolved oxygen in water by all methods has been presented by Schwartz (6); and the problem as applied to boiler feed water has been considered by White, Leland, and Button (10). With such excellent reviews available, it seems unnecessary to discuss the earlier work.

Our problem involves the analyses of power plant waters, particularly where the oxygen concentrations are less than 0.5 ml. per liter. When the author had occasion to calibrate industrial dissolved oxygen recorders, the serious limitations of the starch-iodide titration end point became apparent. The sampling method suggested by Swartz and Gurney (7) was adopted in an effort to correct for the errors from impurities and from the oxygen added in the reagents. When the work was started, the author did not have available the sampling procedure of White, Leland, and Button (10), who collected the dissolved oxygen in the distillate from the sample in an effort to eliminate the nonvolatile substances which affect the accuracy. They used essentially the author's titration method (3).

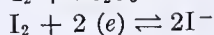
## Iodometry by Electrometric Methods

Willard and Fenwick (11) and Van Name and Fenwick (9) suggested a bimetallic electrode system for use in the electrometric titration of iodine. Foulk and Bowden (1) modified the previous bimetallic electrode titration and described a "dead-stop end point" method for iodometry. Hewson and Rees (2) applied the above method to the determination of iodine liberated by the Winkler reagents.

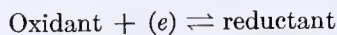
A consideration of the electrometric determination of iodine in solution leads to the following:



or



which is a case of the general class



Kolthoff (4) showed that the potential of the iodine electrode at 25° C. is represented by the equation:

$$E = E_0 + \frac{0.059}{2} \log \frac{[\text{I}_2]}{[\text{I}^-]^2}$$

According to Jones and Kaplan (3), when using a saturated iodine electrode, we have at 25° C.

$$E = 0.5362 - 0.059 \log [\text{I}^-]$$

Kolthoff (4) pointed out that the potential of the iodine electrode depends upon the iodide concentration.

Kolthoff and Furman (5) considered that the thiosulfate tetrathionate electrode is irreversible.

The platinum-saturated calomel electrode is one of the most satisfactory for electrometric oxidation-reduction systems. It seemed that the electrometric method should be particularly applicable to the determination in question.

## Method of Analysis

**SAMPLING.** All oxygen must be removed from the sampling system before sampling is begun.

When the water is at elevated temperatures and pressures it is necessary to avoid flashing of the sample. The flow to the sampling bottles should be controlled by adjusting a valve on the discharge side of an adequate cooling coil.

The temperature of the water at the sampling time should be slightly below that of the room temperature. The temperature of the sample bottle should not be allowed to decrease 1° C. between the time of sampling and the time of analysis. Hence, the temperature at the sampling point preferably should not exceed 30° C. (86° F.).

Three samples are collected in series in sampling bottles equipped with rubber stoppers and with inlet and outlet tubes. The sampling bottles should be slightly oversize and should have narrow mouths designed to accommodate ground-glass stoppers. The end of the glass stoppers should be ground to a semiconic shape to prevent trapping of air bubbles when replacing stoppers. No trace of a gas bubble can be tolerated in the top of the sampling bottles. Two 250-ml. samples and one 500-ml. sample should be taken.

The water sample should enter one of the 250-ml. bottles through a tube extending to the bottom. The sample overflows through an outlet tube at the top into the 500-ml. bottle inlet tube. This overflows into the second 250-ml. bottle. McLeod sampling tubes may be used in place of the bottles. Glass-tube glass butt connections should be provided for all connections. Rubber tubing is used merely to hold the connections in place. At least seven times the total volume of the three sampling bottles should be withdrawn before the sampling is stopped.

**REAGENTS.** The following stock reagents are desirable:

0.1 molar stock sodium thiosulfate solution, 24.82 grams  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  per liter (stored in a brown bottle protected by soda-lime tube). A 0.01 molar sodium thiosulfate solution made up from the above solution and standardized each day by means of a 0.01 molar potassium biiodate solution.

0.01 molar stock potassium biiodate solution, 0.3250 gram  $\text{KIO}_3 \cdot \text{HIO}_3$  per liter.

Manganous chloride solution, 412 grams of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  dissolved in distilled water and made up to 1 liter.

Alkaline-iodide reagent, 700 grams of potassium hydroxide and 150 grams of potassium iodide per liter. The reagent should be free from carbonates, as manganese carbonate does not react with dissolved oxygen. A paraffined glass stopper should be used for the bottle.

Concentrated sulfuric acid of specific gravity 1.84, diluted with an equal volume of water.

**PROCEDURE.** The 500-ml. sample and one of the 250-ml. samples are treated as follows:

Remove the rubber stopper with inlet and outlet tubes. By means of separate pipets rapidly add 2 ml. of the alkaline reagent and then 2 ml. of the manganous chloride reagent. Both reagents sink to the bottom of the bottle without excessive contamination when the tip of the pipet is held below the surface of the sample. Rapidly insert the glass stopper. The slightly air contaminated upper portion of the sample is eliminated.



ated by the overflow when the glass stopper is replaced. Shake thoroughly for 2 minutes and let stand until the precipitate settles three quarters of the height of the sampling bottle. Remove stopper, add 2 ml. of sulfuric acid reagent, replace stopper, and shake thoroughly until the precipitate dissolves.

Iodide solutions are slowly oxidized by air. Accordingly, the glass stopper should not be removed from the sample bottles until all is prepared for the subsequent titration. The titration should be easily completed in less than 5 minutes; hence the error due to the liberation of iodine by air oxidation is very small.

Measure out exactly 250 ml. of the sample from the 250-ml. bottle. Add exactly 250 ml. of untreated water from the other 250-ml. bottle. Then add 0.5 ml. of 0.01 *N* potassium biiodate solution from a pipet. The addition of the standard biiodate solution serves as a check on the titration, particularly when small traces of oxygen are involved in the analysis. Proceed to titrate electrometrically with 0.01 *N* sodium thiosulfate, using a certified buret with a special small tip to give not over 0.02 ml. per drop. Measure out exactly 500 ml. of the sample from the 500-ml. bottle, add potassium biiodate solution in the exact amount used in the 250-ml. sample, and titrate as in the previous case.

The oxygen content for a 250-ml. sample is determined by the difference between the 500-ml. and the 250-ml. sample.

(1 ml. of 0.01 *N*  $\text{Na}_2\text{S}_2\text{O}_3$  is equivalent to 0.0612 ml. of oxygen at 25° C. and 760 mm.)

As an optional procedure, a titration with 0.01 *N* potassium biiodate solution may be found to give slightly greater accuracy. If this method is used, a known excess of 0.01 *N* sodium thiosulfate should be added.

### Electrometric Titration

A 1 × 1 cm. sheet of platinum provided with a suitable lead wire is used as the indicator electrode, and a saturated calomel-saturated potassium chloride system is used as the reference electrode. The two electrodes are mounted in an 800-ml. beaker. Stirring should continue during the entire titration. A mechanical stirrer is desirable. A portable potentiometer with a range of 0 to 1100 millivolts is used to obtain the e. m. f. per ml. of thiosulfate relationship.

It is not necessary to make a complete titration, since the significant abrupt e. m. f. change is easily detected. The

standard thiosulfate solution may be added rapidly until the e. m. f. is approximately 0.3100 volt, and the titration then continued drop by drop until the end point is reached. The end point occurs between 0.290 and 0.260 volt, depending upon the nature of the solution, the pH of the solution, and the concentration of the iodide present. In any instance, at the exact end point one drop of 0.01 *N* thiosulfate solution results in an abrupt drop of over 30 millivolts. The author has found that the end point for the average high-purity water involved in power plant boiler practice occurs at an e. m. f. value of 0.2900 volt for temperatures between 15° and 30° C.

As the end point is approached in iodine solutions, the e. m. f. tends to drift slowly to a higher voltage value immediately after the addition of thiosulfate. At the end point there is no tendency to drift. With an excess of thiosulfate, there is a tendency for the e. m. f. to drift to lower voltage values. As a matter of fact, the use of a properly sensitive galvanometer is all that is required to detect the end point by the drift method; however, this is more critical to operate than the above potentiometer method.

Figure 1 shows a portable unit which the author used to carry out dissolved oxygen tests in the field. Provision has been made for all the necessary pipets, buret, electrodes, sample bottles, beaker, and mechanical stirring equipment. An antimony electrode is also included so that when used with a suitable portable potentiometer, it is also possible to obtain pH measurements.

### Influence of Various Ions

The normal variations in the concentration of sulfate and chloride ions have little influence on the end point. The iodide-ion concentration changes the e. m. f. value of the inflection point, yet the same thiosulfate end point results, irrespective of the iodide concentration. The inflection point

of the curve for the e. m. f. per ml. of thiosulfate occurs at a lower voltage for high iodide concentrations than for low iodide concentrations. This is constant for the author's procedure and hence does not involve any error.

The hydrogen-ion concentration must be controlled within limits. The author's method is sufficiently standardized so that the hydrogen-ion concentration is held within the desired limits. More thiosulfate is required to reduce all of the iodine to iodide as the concentration of hydrogen ion is increased. The more nearly the solution is held to 7.0 pH, the less is the effect upon the thiosulfate end point.

### Precision of the Method

The high sensitivity of the change at the end point is noteworthy. One drop of thiosulfate from a specially small buret tip, which has been found to be equivalent to 0.02 ml., results in a 30-millivolt change. Thus the author was able to detect the presence of 0.0000016 gram of oxygen in the 250-ml. sample. This is roughly 0.0064 part by weight of

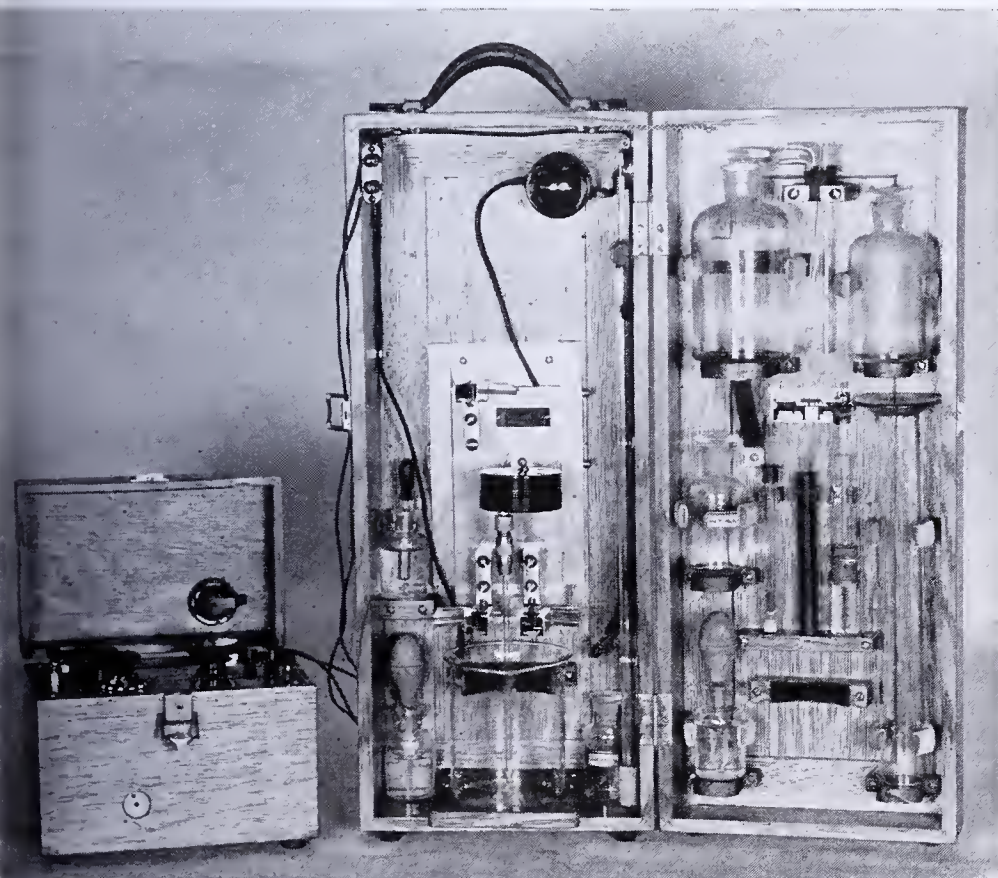


FIGURE 1. PORTABLE UNIT



oxygen per million parts by weight of water (1 part in about 156,000,000).

Tests indicate that the limit of error of the titration is  $\pm 0.001$  ml. of oxygen at 25° C. and 760 mm.

### Advantages of the Method

The author has used this equipment extensively in connection with power plant tests and has found the following advantages in making dissolved oxygen determinations:

The use of the simplified electrometric titration procedure eliminates the temperature, starch quality, and personal equation errors of the starch-iodide method.

The analysis is based upon a difference determination whereby the influence of dissolved oxygen in the reagents, small ionic variations of foreign substances, secondary reactions, loss of dissolved oxygen by displacement, possible

contamination of the sample by air when the reagents are added, and temperature variations are minimized.

The complete equipment can be made in portable form.

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# Measurement of Plastic Properties of Bituminous Coals

## Comparison of Gieseler and Davis Plastometer and Agde-Damm Dilatometer Methods

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THE torsional principle—that is, the measurement of resistance to shear caused by movement of a stirring device within the heated coal charge—was first applied in 1931 by Davis (5) to the determination of the "plastic" properties of bituminous coking coals. Since then, this general principle has been employed in various forms of other instruments (9-13). Although the later designs of the Davis plastometer have incorporated a few minor changes to ensure smoothness in operation and improve general appearance, the original instrument, after more than seven years of continued use, has proved satisfactory. It has been found, however, that the procedure (5-8) gives more uniform test results when modified (3), especially by the use of a larger sample of representative coal and by operation of the retort at a slower speed of rotation, and that "minor limitations lie in the difficulties of determining accurately small changes during the period of greatest fluidity and extremely high resistances, above 63.4 kg.-cm. (55 pound-inches) shown by certain coals." These difficulties have been overcome by the use of tension springs with a sensitivity of less than 0.23 kg.-cm. (0.2 pound-inch), during the period of greatest fluidity, which permit accurate measurements of resistances up to 149.8 kg.-cm. (130 pound-inches).

In the Davis plastometer method (5) the coal charge as a whole is rotated and stirred; the property measured is the resistance to shear of the partly fused coal adhering to the inner periphery of the retort. In the Gieseler plastometer method (9) the coal is static at the start, and later stirring is proportional to the fluidity of the coal. Accordingly, with increase in fluidity of the heated coal are noted (a) a decrease in resistance, or torque, measured in kilogram-centimeters, in the Davis rotary retort, and (b) an increase of the rate of rotation of the stirring shaft in the Gieseler stationary retort.

In (a) the resistance is created by the movement of the coal in the retort against the rabble arms on the inside shaft, which is prevented from free rotation by the tension springs; in (b) the rotation of the stirring shaft is caused by application of a constant force on the loading pan.

Gieseler (9) criticized the method of Davis (5) because the coal is heated under conditions corresponding to those of a rotary retort, permitting volatile matter and tar to escape more freely than in a coke oven. Gieseler (9) made the broad assertion that all methods for the determination of plasticity in which the coal is not prevented from expanding are unsatisfactory, quoting a statement from Davies and Mott (4) that a "coal which is free to expand loses volatile matter readily and plasticity ends at a comparatively low temperature." Davies and Mott (4) showed, however, that the temperature of solidification, termed by them the "end of plasticity", is higher than the temperature of final expansion as determined by the Sheffield laboratory coking test on a number of the better coking coals.

At the beginning of the solidification of a melted coal mass into semicoke a coal rapidly loses its fluidity. At this stage the Gieseler instrument naturally shows with increasing temperature less and less movement of the stirring shaft per unit of time, and as semicoke formation proceeds this movement falls off rapidly to zero. The apparent discrepancy in the interpretation of the "end of plasticity" is, therefore, purely one of definition. The temperature limits of the plastic range for the Davis plastometer test are defined as the difference between the temperature at which resistance develops and that at which resistance ends. This latter temperature is some degrees higher, the magnitude varying with different coals, than that of maximum resistance at solidification, which, in turn, is higher than the temperature



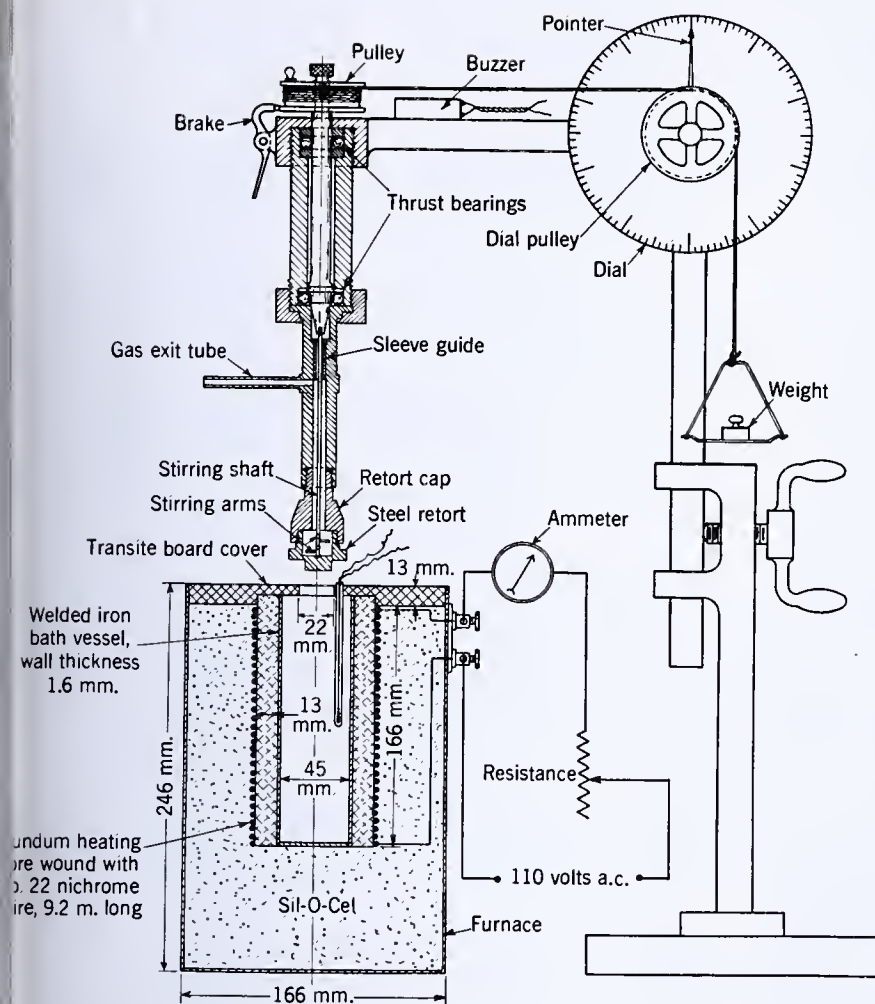


FIGURE 1. MODIFIED GIESELER APPARATUS

the end of high fluidity or the start of solidification of the softened coal mass into semicoke. Furthermore, Gieseler has shown (9) that the end of the softening zone determined by his instrument agrees closely with that obtained by his penetrometer method on the same coals. This temperature, as shown in Table II of the present paper, agrees more nearly with the solidification temperature but always lies below the end of the plastic-range temperature, as determined by the Davis plastometer. The difference in the temperatures for the "end of the plastic range" in the Gieseler and Davis plastometer methods is to be expected, therefore, from the operating characteristics of the two instruments.

#### Development of the Modified Gieseler Plastometer

Experience in this laboratory with retorts designed according to descriptions by Gieseler (9) and Jung (10) showed difficulties in charging and uniform packing of the coal sample. The "personal equation" involved in the tedious method of packing the coal charge employed by these authors was largely eliminated in the present work by the use of a specially designed loading device and a simplified retort threaded on the outside wall at the top and without a removable cap at the bottom. Figure 1 is a sectional drawing of this retort, on a somewhat larger scale than that of the rest of the apparatus.

The retort is 21 mm. in inside diameter and 16 mm. in depth. In testing strongly contracting coals a steel pin 1.6 mm. in diameter is inserted through a hole in the retort at a point 5 mm. from the top and to a distance of 5 mm. radially toward the center from the inside wall. Without this pin arrangement the stirring shaft carries the contracted coal charge around and thereby falsely indicates a highly fluid mass. At the same time, the pin arrangement constitutes an improvement over the sieve-plate cover first used at the top of the retort, since

the binding between the stirrer shaft and the sieve plate caused by the accumulation of partly carbonized heavy tars is entirely eliminated.

A radial type of ball spindle bearing assembly taking a horizontal thrust only was first used. Because of high friction in this bearing, a weight of 145 grams on the loading pan was required for satisfactory operation. Except for the fusion temperatures, which showed the same order of agreement, the data obtained with this bearing and 145 grams on the loading pan were less concordant than those obtained with the new ball-bearing assembly shown in Figure 1. This latter bearing takes both a vertical and horizontal thrust and shows but little friction in its operation. A 20-gram weight on the 18.7-gram loading pan is sufficient to cause uniform rotation of the stirring shaft in the empty retort, no rotation in the coal charge until initial softening of the coal is reached, and a smooth movement during passage through the preplastic and plastic temperature ranges.

A comparative study of different mesh sizes of coal—passing through 20-, 35-, and 60-mesh (Tyler sieves)—showed that the 35-mesh size was the most suitable. The length of the high fluidity temperature range was not affected by changes in the particle size of the coal. However, the 20-mesh size showed a higher maximum fluidity at a slightly higher temperature than the 35-mesh coal. This difference may be attributed to the fact that more time is required to heat through the larger size particles; in consequence, more fluid material would result at the time of maximum fluidity. The 60-mesh size tended to become frothy and swell out of the retort, causing erratic indications. Since the capacity



FIGURE 2. LOADING DEVICE FOR PACKING COAL CHARGE

of the retort, 4.0 to 4.2 grams of coal, is believed to be too small to permit use of a representative 20-mesh coal sample, the 35-mesh size is taken as standard. This latter size,  $<0.417$  mm., corresponds to that used by Jung (10)— $<0.4$  mm.

Instead of the equimolecular mixture of sodium and potassium nitrates (9, 10), with its attendant danger of explosions, a bath consisting of 750 grams of Wood's metal and 680 grams of "half and half" solder and with a melting point of  $138^{\circ}$  C. is used. The temperature in the center of the coal charge in the retort was found to be lower by  $4^{\circ}$  C. or less



TABLE I. ANALYSES OF COALS, AS RECEIVED BASIS

Coal No.	Coal Bed	Dry, Mineral Matter-Free Volatile Matter %	Proximate			Ash %	Hydrogen %	Ultimate			Sulfur %	Heating Value—	
			Moisture %	Volatile matter %	Fixed carbon %			Carbon %	Nitrogen %	Oxygen %		B. t. u./lb.	Cal./gram
50	Upper Kittanning (unwashed) (Bethlehem No. 73 Mine)	17.9	1.8	16.9	72.0	9.3	4.5	79.1	1.2	3.6	2.3	13,860	7700
51	Upper Kittanning (washed) (Bethlehem No. 73 Mine)	18.5	2.2	17.3	72.0	8.5	4.5	80.2	1.4	4.2	1.2	13,980	7767
XP-3	Miller "B" or Lower Kittanning (Indian Creek No. 4 Mine)	27.3	0.6	25.5	65.1	8.8	4.8	79.6	1.3	3.5	2.0	14,140	7856
51B	70% coal 28C and 30% coal 51	31.4	1.6	29.4	62.5	6.5	5.0	79.5	1.6	6.3	1.1	14,050	7806
50B	70% coal 28C and 30% coal 50	32.3	2.3	30.0	61.2	6.5	5.2	78.8	1.5	6.8	1.2	14,000	7778
51A	80% coal 28C and 20% coal 51	33.0	1.9	30.9	61.2	6.0	5.2	79.3	1.6	6.8	1.1	14,010	7783
53	Pond Creek (Majestic Collieries)	33.9	2.7	31.9	61.1	4.3	5.3	80.5	1.5	7.7	0.7	14,290	7939
50A	80% coal 28C and 20% coal 50	34.1	1.8	31.8	60.1	6.3	5.2	78.8	1.5	7.0	1.2	14,080	7822
28C	Pittsburgh (Warden Mine)	38.1	1.9	35.6	56.9	5.6	5.5	78.9	1.5	7.6	0.9	14,080	7822
52	Pittsburgh (Bruceton Mine)	40.1	2.4	36.6	53.2	7.8	5.1	75.8	1.5	8.2	1.6	13,560	7533
54	High Splint (Closplint Mine)	40.1	3.3	37.5	55.5	3.7	5.5	78.3	1.4	10.6	0.5	13,870	7706

over the preplastic and plastic temperature ranges than that at the same level in the bath on the outside wall of the retort. This temperature difference is almost identical with that found by Jung (10) for his low-form retort in the nitrate bath. To compensate for small losses from volatilization during use, small quantities of tin are added as required to maintain the proper bath level. To minimize oxidation of the bath surface a layer of powdered charcoal may be added.

The test procedure is as follows:

The open retort with stirring shaft in place is mounted in the loading device (Figure 2) and is charged with 4.2 grams of coal, passing 0.417 mm.; the charge is then compressed for 15 minutes under a 10-kg. load. This manner of charging gives a charge density of 0.87 gram per cc. (54.3 pounds per cubic foot), which is within the range used in commercial coke ovens. The retort cap is screwed on the retort and into the head above, as shown in Figure 1. The assembled apparatus is then lowered into the bath, preheated to 340° C., until the gas exit tube rests just above the top of the furnace. The Transite cover is next

perature, and pointer movement are made at 1-minute interval. During the testing of many coals it is necessary to rewind the thread on the stirring shaft pulley a number of times. This may be done quickly without disturbing the test by loosening the milled nut on the pulley shaft and turning the pulley backward. During the testing of coals showing high fluidity the rate of pointer movement over the dial becomes too high to permit continuous readings. The fluidity of such coals is measured accurately by the help of a brake acting on the stirring shaft pulley. In case of pointer movement too rapid to permit continuous readings, the brake is first set, then released, and after the pointer movement becomes uniform its rate per revolution is timed with a stop watch. These periodic readings are repeated until the pointer movement is again slow enough to permit continuous readings.

From the observed times, temperatures, and dial readings the corresponding number of pointer revolutions is calculated in dial divisions per minute. These latter values are plotted as ordinates against temperatures in degrees Centigrade as abscissas (Figures 3 and 4). The dial divisions per minute

corresponding to the fluidity of the coal increase to a maximum and then decrease to zero.

Table I shows the coal number, coal bed, dry mineral matter-free volatile matter percentages of the coals in the order of decreasing rank (1), proximate and ultimate analyses and heating value of the seven coals and four blends tested.

Table II compares the characteristic temperature points and degrees of fluidity obtained by the modified Gieseler plastometer test method and by the Agde-Damm dilatometer and Davis plastometer test methods (3). The seven coals and four blends are arranged in the order of decreasing rank (1), as Table I. The same heating rate, 3° C. per minute, was used throughout the preplastic and plastic temperature ranges in the three methods. The characteristic temperature and resistance values reported for the Agde-Damm and Davis methods are those defined previously (3). In expressing corresponding data for the Gieseler plastometer there are taken (a) the initial softening temperature corresponding to 0.1 dial division (1/1000 of the dial

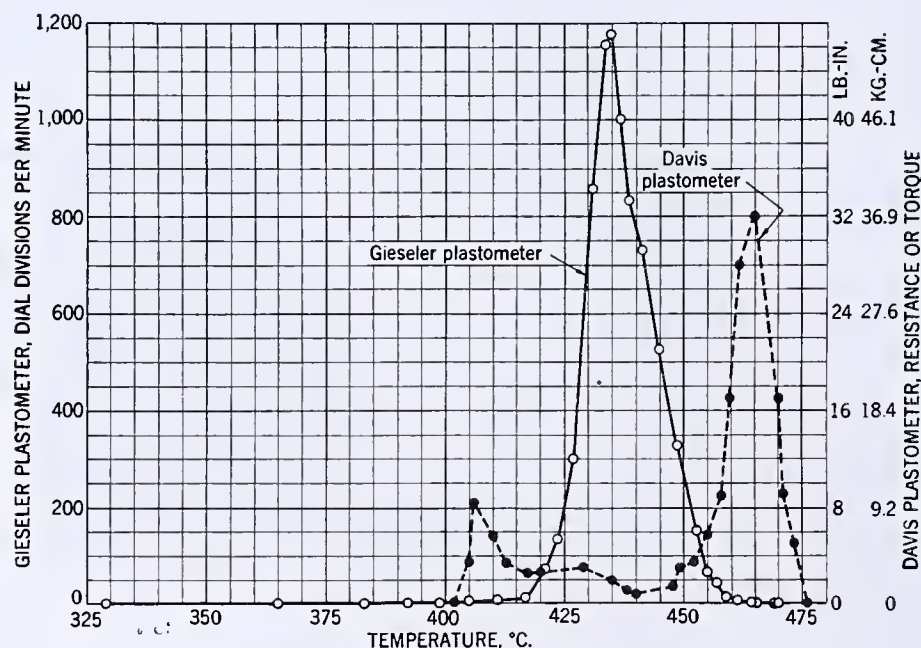


FIGURE 3. PLASTIC PROPERTIES OF HIGH-VOLATILE A COAL 51A

dropped in place and the thermocouple installed with its hot junction against the outside wall of the retort at a position opposite the center of the coal charge.

Introduction of the cold apparatus so reduces the bath temperature that about 10 minutes' time is required to bring it back to 340° C., after which the heating rate is maintained at 3° C. per minute. At the initial softening temperature of the coal the loaded pan starts to fall and continues falling to the end of the test. This initial softening temperature is taken at the first appreciable pointer movement—i. e., 0.1 dial division on the 100-scale-division dial. From this point on readings of time, tem-

perature, and pointer movement are made at 1-minute interval. During the testing of many coals it is necessary to rewind the thread on the stirring shaft pulley a number of times. This may be done quickly without disturbing the test by loosening the milled nut on the pulley shaft and turning the pulley backward. During the testing of coals showing high fluidity the rate of pointer movement over the dial becomes too high to permit continuous readings. The fluidity of such coals is measured accurately by the help of a brake acting on the stirring shaft pulley. In case of pointer movement too rapid to permit continuous readings, the brake is first set, then released, and after the pointer movement becomes uniform its rate per revolution is timed with a stop watch. These periodic readings are repeated until the pointer movement is again slow enough to permit continuous readings.



TABLE II. COMPARISON OF AGDE-DAMM, GIESELER, AND DAVIS TEST DATA

Coal No.	Coal Bed	Dry, Mineral Matter—Free Volatile Matter %	Initial Softening Temperature		Fusion Temperature				Maximum Fluidity				Solidification				End of Plastic Range Gieseler plastom-eter ° C.	Davis plastom-eter ° C.		
			Agde-Damm dilatometer, initial contraction tem-perature ° C.	Gieseler dilatometer, 0.1 dial division ° C.	Agde-Damm dilatometer, initial expansion tem-perature ° C.	Gieseler dilatometer, 5.0 dial divisions per minute ° C.	Davis dilatometer, resistance velops ° C.	Gieseler dilatometer, final expansion tem-perature ° C.	Gieseler dilatometer, maximum movement ° C.	Davis dilatometer, minimum resistance ° C.	Gieseler dilatometer, 5.0 dial divisions per minute ° C.	Davis dilatometer, maximum resistance ° C.	Gieseler dilatometer, 5.0 dial divisions per minute ° C.							
50	Upper Kittanning (unwashed) (Bethlehem No. 73 Mine)	17.9	423	427	...	...	443 <sup>a</sup>	...	...	451	1.2	...	...	...	467 <sup>a</sup>	...	...	482	...	
51	Upper Kittanning (washed) (Bethlehem No. 73 Mine)	18.5	427	427	...	...	442 <sup>a</sup>	...	...	459	0.8	...	...	...	472 <sup>a</sup>	...	...	482	...	
XP-3	Miller "B" or Lower Kittanning (Indian Creek No. 4 Mine)	27.3	355	354	410	406	406	399	426	431	315	440	0.6	(0.5)	443	495	61.1	(53)	446	507
51B	70% coal 28C and 30% coal 51	31.4	346	351	418	406	406	405	434	433	706	412	1.7	(1.5)	456	454	79.5	(69)	466	472
50B	70% coal 28C and 30% coal 50	32.3	347	346	414	407	405	405	424	432	577	435	0.8	(0.7)	456	464	38.0	(33)	462	470
51A	80% coal 28C and 20% coal 51	33.0	342	347	415	406	402	402	426	435	1177	440	1.2	(1.0)	461	465	36.9	(32)	469	476
53	Pond Creek (Majestic Collieries)	33.9	349	348	416	405	410	401	451	429	1250	424	0.6	(0.5)	461	477	21.3	(18.5)	462	491
50A	80% coal 28C and 20% coal 50	34.1	342	349	408	404	399	399	420	436	1818	435	0.2	(0.2)	465	467	34.6	(30)	475	478
28C	Pittsburgh (Warden Mine)	38.1	346	341	403	405	401	401	430	426	583	426	0.0	(0.0)	447	466	27.6	(24)	449	475
52	Pittsburgh (Bruceston Mine)	40.1	334	336	401	397	395	395	426	420	706	432	0.2	(0.2)	433	459	34.0	(29.5)	435	464
54 <sup>b</sup>	High Splint (Closplint Mine)	40.1	352	356	...	...	394 <sup>a</sup>	410	424	426	6.0	443	0.2	(0.2)	439 <sup>a</sup>	456	10.9	(9.5)	445	474

<sup>a</sup> Owing to low fluidity of coals 50, 51, and 54, fusion and solidification temperatures are taken at 0.5 dial division per minute.

<sup>b</sup> Coal 54 tested with pin in retort.

<sup>a</sup> Owing to low fluidity of coals 50, 51, and 54, fusion and solidification temperatures are taken at 0.5 dial division per minute.  
<sup>b</sup> Coal 54 tested with pin in retort.

the Gieseler test gives values consistent with the corresponding characteristic temperature points established by the other two methods. Furthermore, it seems expedient to define arbitrarily for comparative purposes a temperature range of high fluidity, as has been done by Gieseler ("zone of greatest plasticity", 9) and by Brewer and Atkinson ("high fluidity range", 3). Table III gives such a comparison for the more fluid coals tested. Here the temperature limits are defined in the Gieseler test for the period during which the pointer movement is 50 dial divisions or more per minute and for the Davis test while the fluid coal shows a resistance of 2.3 kg.-cm. (2 pound-inches) or less.

Discussion of Results

Table II shows that the initial softening temperatures by the Agde-Damm and Gieseler methods are in excellent agreement. On account of the use of a lighter, flat-nosed plunger as compared with the heavier, round-nosed plunger previously described (3), the fusion temperatures by the Agde-Damm method are somewhat higher than the closely agreeing values obtained by the two plastometer methods. As has been pointed out by Brewer and Atkinson (3) among others, the Agde-Damm final expansion temperature does not correspond to the maximum fluidity state in all coals. Fair agreement, however, is noted for some coals between the maximum fluidity temperatures by all three methods. For reasons discussed above, the operating characteristics of the Gieseler and Davis plastometers may be expected to yield somewhat different values for the temperatures of maximum fluidity, solidification, and the end of the plastic range. The agreement of data obtained by the plastometer methods for many of the coals, particularly for the temperatures of maximum fluidity and solidification, are nevertheless satisfactory.

In commercial coke-oven practice low-volatile bituminous coals 50 and 51 are known to exhibit dangerous expansion properties. These coals, when tested in the experimental sole-heated and slot ovens (2), showed expansions of more than 20 per cent, based on a charge density of 870 kg. per cubic meter (54.3 pounds per cubic foot). Except for the Agde-Damm initial contraction temperature, they show no characteristic temperature points throughout the usual preplastic and plastic temperature ranges, when heated at the normal rate—i. e., 4.8° C. per minute over-all and 3° C. per minute through the preplastic and plastic temperature ranges—in either the Agde-Damm dilatometer or Davis plastometer test methods. At higher heating rates or at normal heating rates above 500° C. fusion of these coals takes place—for example, coal 50 at an over-all heating rate of 7.85° C. per minute showed a plastic range of 470° to 519° C. in the Davis plastometer. Although an increased rate of heating is known to be a contributing factor in promoting "plasticity" in all coals, it is believed that there are other equally important causes, not yet fully established, responsible in the low-volatile bituminous coals. The Gieseler tests on coals 50 and 51 show small, but appreciable, values for maximum fluidity. Similar results have been obtained by Gieseler (9) on a Ruhr coal containing 17.3 per cent of pure-coal volatile matter.

Medium-volatile bituminous coal XP-3 (Table II), in contrast to low-volatile bituminous coals 50 and 51, exhibits well-defined plastic properties. This coal showed an expansion of 11.9 per cent, based on a charge density of 870 kg. per cubic meter (54.3 pounds per cubic foot), in the sole-heated oven (2). The remaining eight coals and blends, 51B-54, inclusive, shown in Table II, are all high-volatile A bituminous coals and representative of those used in commercial coking practice. The maximum fluidity shown by the Gieseler test for the eleven coals in Table II increases to



a maximum and then falls with decreasing rank of the coals. Two apparent exceptions to this general relationship are noted.

That this relationship is not strictly linear is to be expected when the possible different types of coal present in the samples are considered. This fact is well illustrated by the work of Gieseler (9), which showed that the maximum fluidity (1) increased in regular order from 1 to 200 angular degrees for six Ruhr coals ranging in pure-coal volatile matter from 17.3 to 26.0 per cent; (2) increased, with one exception, but with much lower values, from 14 to 39, for four Lower Silesia coals with pure-coal volatile matter from 24.7 to 34.0 per cent; and (3) decreased regularly from 600 to 7 for four Upper Silesia coals with pure-coal volatile matter from 29.6 to 36.2 per cent. If the four Lower Silesia coals are rearranged within those of the Ruhr and Upper Silesia coals in the order of increasing pure-coal volatile matter percentages, a number of apparent exceptions would be noted among the fifteen coals in the general relationship stated above.

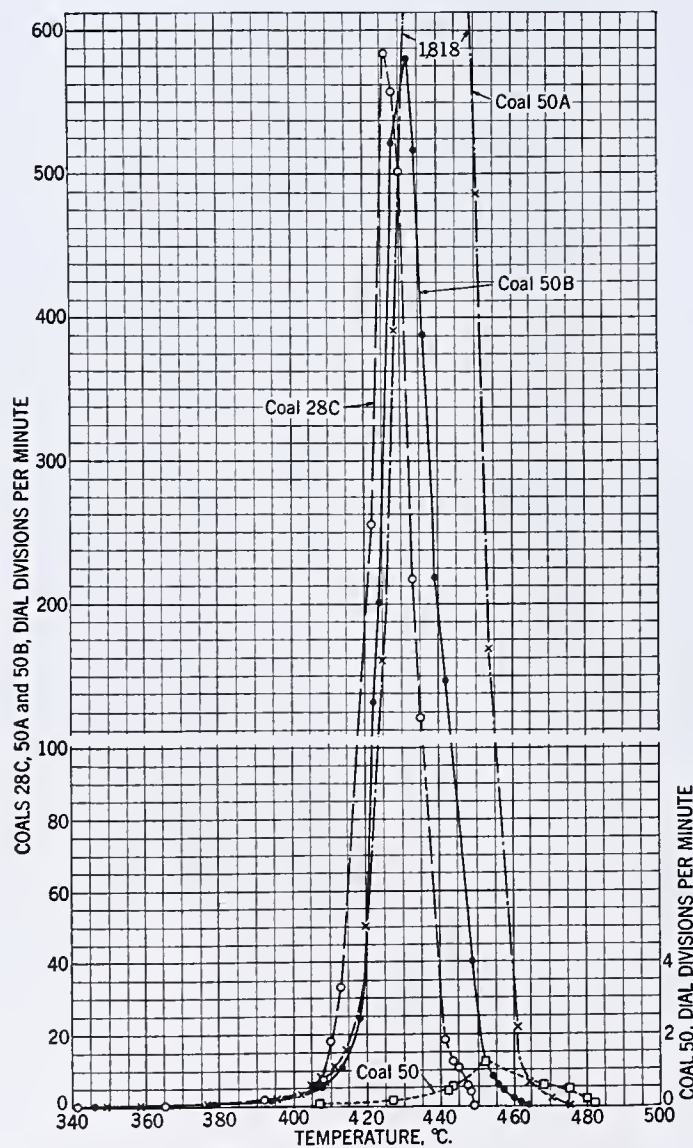


FIGURE 4. PLASTIC PROPERTIES OF COALS 28C, 50, AND THEIR BLENDS, COALS 50A AND 50B

It is evident, therefore, when plastic properties are classified according to rank of the coal, that the types of coal represented must be also considered. As further proof of this, it may be noted from Table II that coals 52 and 54 are of the same rank, each containing 40.1 per cent of dry mineral matter-free volatile matter, but that the maximum fluidity of coal 52 is much greater than that of coal 54. Coal 52

TABLE III. TEMPERATURE RANGE OF HIGH FLUIDITY

Coal No.	Coal Bed	Gieseler, 50 Dial Divisions or More, Pointer Movement ° C.	Davis, 2.3 Kg.-Cm. (2 Pound-Inches) or Less, Resistance ° C.
XP-3	Miller "B" or Lower Kittanning (Indian Creek No. 4 Mine)	419-441	426-460
51B	70% coal 28C and 30% coal 51	417-447	412-420
50B	70% coal 28C and 30% coal 50	421-444	426-442
51A	80% coal 28C and 20% coal 51	420-456	420-446
53	Pond Creek (Majestic Collieries)	417-451	421-444
50A	80% coal 28C and 20% coal 50	421-458	422-450
28C	Pittsburgh (Warden Mine)	414-437	410-455
52	Pittsburgh (Bruceton Mine)	411-430	419-446

showed from petrographic analyses a content of 84 per cent bright, 13 per cent semisplint, and 3 per cent splint, whereas coal 54 gave 33 per cent bright, 14 per cent semisplint, and 53 per cent splint coal. Carbonization tests at 900° C. in the B. M.-A. G. A. 45.7-cm. (18-inch) retort of the predominantly bright coal 52 and of the high-splint coal 54 gave cokes which showed, respectively, cumulative percentages of 67.4 and 63.2 for the 3.81-cm. (1.5-inch) shatter test and 38.8 and 37.7 for the 2.54-cm. (1-inch) tumbler tests.

Table III shows the temperature ranges of high fluidity, estimated as there defined, for the Gieseler and Davis plastometer methods. The temperature values show good agreement for the beginning of high fluidity, while those for the end of high fluidity are less concordant. The reason for the poorer agreement in the latter values undoubtedly lies in differences inherent in the two test methods. It is well known that the actual amount of fluid material present at any one time in the high-fluidity range of a melted coal mass may vary with test conditions, and these are certainly affected by the manner of stirring.

Figure 3 compares the plastic properties of coal 51A determined by the two plastometer methods. The curves are representative of the type obtained for coals showing considerable fluidity.

Figure 4 shows the Gieseler curves for coals 28C, 50, and their blends, 50A and 50B. The ordinate scale for coal 50 is tenfold that of the corresponding portion of the ordinate scale for coals 28C, 50A, and 50B, and the ordinate scale for these three coals for dial readings up to 100 divisions per minute 2.5 times its value above 100 divisions per minute. These enlargements in scale of plotting were made to bring out more clearly the lower ordinate values representing low fluidity. The maximum fluidity of coal 50 is at only 1.2 and that of coal 28C at 583 dial divisions per minute. Coal 50B (70 per cent moderately fluid coal 28C and 30 per cent slightly fluid coal 50) shows nearly the same fluidity as coal 28C—i. e., 577 compared with 583 dial divisions per minute. Coal 50A (80 per cent coal 28C and 20 per cent coal 50), however, shows an extremely high fluidity, 1818 dial divisions per minute. The additional 10 per cent of coal 28C in coal 50A, above that in coal 50B, not only increases the fluidity beyond that of either coal of the blend, but shows also this higher fluidity at a slightly higher temperature than shown by coal 28C or by coal 50B.

One might suppose that these differences are due to the use of a higher heating rate through the plastic range of coal 50A than was used for coal 50B. A number of repeated tests showed, however, that this was not the explanation. In fact, variation of the heating rate through the plastic range for the two blended coals between the limits 2.44° and 3.21° C per minute still gave fluidity values of decidedly higher magnitude for coal 50A, even when results obtained at the lower heating rate for this coal were compared with those for coal 50B at the higher heating rate. Similar results are



bserved in tests with blended coals 51A and 51B. The high maximum fluidity value shown by the blends, 51B, 50B, 51A, and 50A, in comparison with those of the constituent coals of these blends, is a property in harmony with the well-known fact that many properties exhibited by blends are not a mean of the same properties shown by the constituent coals in the blend. Often a blend exhibits a particular property, or properties, to a greater degree than either constituent coal. This is well illustrated by the maximum fluidity values of coals 51A and 50A.

Summary and Conclusions

A modified Gieseler plastometer and test procedure have been developed. Plasticity data obtained by this method are compared with data found by the Agde-Damm dilatometer and Davis plastometer methods.

Considering the differences in operating characteristics of the three instruments, good agreement is shown on typical temperature points and on degrees of fluidity. The modified Gieseler plastometer method has the advantages of covering both the preplastic and plastic temperature ranges, of measuring the small degree of fluidity shown by low-volatile bituminous coals, and of indicating the relative fluidity between coals. This relative fluidity reaches a maximum in high-volatile A bituminous coals of about average volatile-matter content. The excellent agreement between the initial softening temperatures determined by the Agde-Damm and Gieseler test methods substantiates the generally accepted explanation that the "initial contraction temperature" (Agde-Damm) indicates the beginning of a gradual softening of the coal particles. The Gieseler test shows that such softening does take place.

The characteristic temperature points in the plastic temperature range determined by the three test methods measure particular stages of the fusion of the coal and its solidification to semicoke. Except where the operating characteristics of the three instruments necessarily indicate certain differences due to the mode of measurement, a good order of agreement between data obtained by the three test methods

is shown. Alleged arguments against the imperfections of any one method largely disappear when one considers the proper limitations to which this method must be confined in actual use.

Acknowledgments

The authors desire to express their sincere thanks to J. D. Davis for many helpful suggestions during the course of the work. Grateful acknowledgments are made to H. M. Cooper, under whose direction were made the coal analyses shown in Table I, and to G. C. Sprunk and H. J. O'Donnell for their petrographic analyses of coals 52 and 54.

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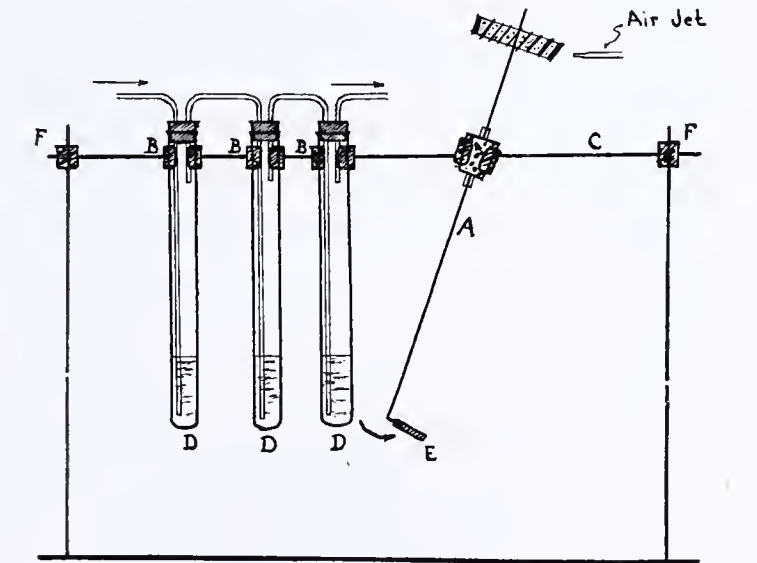
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A Simple Vibrator

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WHEN gases are being passed through an absorption train, it is frequently difficult to maintain a uniform flow of gas through the system. This difficulty may be easily overcome if by some means the absorption tubes are caused to vibrate gently.

A simple and inexpensive type of vibrator suitable for this purpose is illustrated in the diagram. An ordinary laboratory stirrer, A, having an L-foot, is rigidly attached to the cross bar, C, which is common to the absorption tubes. The absorption tubes, D, are mounted on the cross bar by means of buret clamps, B. The cross bar in turn is rigidly fixed to the standards by means of the double clamps, F. On the L-foot of the stirrer there is a short piece of gum rubber tubing, E, extending beyond the glass. The stirrer is slanted at such an angle that when rotated E strikes the lower end of the last tube. The vibration thus established is carried through the cross bar, C, to the rest of the tubes in the train. More efficient operation is obtained if the tubes, D, are mounted near their tops and if the cross bar is attached near



the top of the standards. It may be necessary to apply mineral oil to the rubber foot, E, for proper operation.

Use of this easily made vibrator leads to a flow of small gas bubbles through the absorption train.



# Composition of High-Solvency Hydrocarbon Thinners

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Data gathered by ten laboratories, working in six cooperating groups, show that a recent method of estimating the aromatics, naphthenes, and paraffins in substantially olefin-free hydrocarbon thinners of the high-solvency type provides adequate precision and accuracy in the determination of aromatics. Naphthenes and paraffins are found less accurately, but aromaticity is apparently the important property. Accuracy and precision were checked by analyzing commercial thinners, blending pure hydrocarbons according to these results, and analyzing the blends; and by comparing viscosities of resin solutions in each pair of thinners.

As it stands, the method is not recommended for the proximate analysis of low-solvency thinners.

IN 1938 the Philadelphia Paint and Varnish Production Club developed a rapid method for the proximate analysis of hydrocarbon thinners derived from petroleum and coal tar (6). To check the precision of the method, several cooperating laboratories obtained results showing satisfactory agreement when analyzing six commercial thinners, of the usual boiling ranges, whose aromatic contents exceeded 35 per cent. Low-solvency naphthas, however, of the lacquer diluent (varnish maker's and painter's naphtha) and "mineral spirits" types did not lend themselves to good precision of analysis, and hence work is now in progress to refine the procedure.

Accuracy of the method was tested by only one cooperator. Further, it was felt that a family of curves which were used to determine naphthenic and paraffinic content permitted too great an error in selection and reading. Hence, to provide greater accuracy, as well as to prove the utility of the method for evaluating the higher solvency naphthas, the present cooperative work was undertaken.

As it stands, the proximate analytical method requires the removal of aromatic hydrocarbons present in the usual commercial thinners by whirling rapidly, in a 125-cc. glass-stoppered Erlenmeyer flask, 10 cc. of thinner with 20 cc. of c. p. 20 to 30 per cent sulfur trioxide fuming sulfuric acid. A good emulsion should be obtained. During the first 5 minutes of contact the flask should be cooled by immersion in ice water. A second 5 minutes of rapid whirling in the air, with the stopper set loosely, is followed by 30 minutes of settling, decantation of a few drops of raffinate (now saturated with sulfur dioxide), and the determination of the refractive indices at 20° C. of both raffinate and original thinner.

Assuming (6) the average refractive index of the aromatics present in substantially olefin-free commercial thinners boiling above 95° C. and below 200° C. to be 1.4960, and cor-

recting for the dissolved sulfur dioxide in the acid raffinate the aromatic fraction,  $X$ , is found according to the equation

$$1.4950 X + \text{refractive index of raffinate} (1 - X) = \text{refractive index of thinner}$$

Naphthenic and paraffinic contents of the nonaromatic fraction are read from one of a family of curves corresponding to the boiling range of the thinner in question (6, 7).

One means of checking the accuracy of the method is to compare the determined composition and solvency of commercial thinners with those of corresponding synthetic blends of pure aromatics, naphthenes, and paraffins of the same boiling ranges. Accordingly, the present cooperators have analyzed three commercial petroleum naphthas whose evaporation rates are just faster than toluene—thinners C, D, and F—and also synthetic blends made from toluene, 98 per cent pure methylcyclohexane, and pure *n*-heptane, according to the median results obtained for these naphthas by the cooperating laboratories in last year's work (6).

Percentages of aromatics, by volume (3, 5), were found in the usual manner. Naphthenes and paraffins, however, were determined in the nonaromatic fraction from a nomogram (Figure 1) adapted from the family of curves previously referred to (6, 7), but differing in that the "average boiling point", instead of the boiling range, of the thinner is used. It is felt that the average of the 10, 20, 30, 70, 80, and 90 per cent points of an A. S. T. M. distillation more closely defines the average molecular weight of a thinner and hence the refractive indices of the major naphthenic and paraffinic components, than does the boiling range—i. e., the spread from A. S. T. M. initial to A. S. T. M. final boiling point. Average boiling point has been found to correspond closely to both the 50 per cent point and the so-called "weighted average."

TABLE I. ANALYSIS OF THINNERS

	C %	D %	F %
Aromatics (volume per cent of toluene)	38.0	8.8	67.7
Naphthenes (volume per cent of methylcyclohexane)	33.5	15.9	17.1
Paraffins (volume per cent of <i>n</i> -heptane)	28.5	75.3	14.1

TABLE II. COMPOSITION OF HIGH-SOLVENCY NAPHTHAS

Thinner	1	2	3	4	5	6	Av.	Av. Deviation
(Cooperators 1 to 6)								
Per Cent Aromatics by Volume								
Commercial C	38.2	38.5	38.0	37.0	38.4	38.7	38.1	0.43
Synthetic C	37.7	37.2	38.2	37.6	38.1	39.0	38.0	0.47
Commercial D	8.2	8.4	8.2	9.2	8.6	10.3	8.8	0.92
Synthetic D	9.0	8.8	9.1	8.4	9.5	9.6	9.1	0.33
Commercial F	69.4	67.8	69.6	68.6	69.0	68.7	68.9	0.48
Synthetic F	67.6	66.7	67.4	66.4	67.5	65.7	66.9	0.62
Per Cent Naphthenes by Volume								
Commercial C	34.5	34.9	35.3	33.4	33.7	33.9	34.3	0.7
Synthetic C	28.2	31.4	28.4	26.8	27.2	24.0	27.7	1.7
Commercial D	21.1	19.6	21.3	15.0	18.2	14.0	18.2	2.4
Synthetic D	9.1	11.0	11.5	8.2	7.5	8.3	9.3	1.3
Commercial F	17.7	18.2	17.6	17.9	18.6	18.7	18.1	0.4
Synthetic F	12.9	15.9	13.8	14.5	13.8	17.4	14.7	1.3
Per Cent Paraffin by Volume								
Commercial C	27.3	26.6	26.7	29.6	27.9	27.4	27.6	0.8
Synthetic C	34.1	31.4	33.4	35.6	34.7	37.0	34.4	1.4
Commercial D	70.7	72.0	70.5	75.8	72.2	74.8	72.7	1.8
Synthetic D	82.0	80.2	79.5	83.4	83.0	82.0	81.7	1.2
Commercial F	13.0	14.0	12.8	13.5	12.4	11.6	12.9	0.6
Synthetic F	19.5	17.4	18.8	19.1	18.7	16.9	18.4	0.8

<sup>1</sup> E. C. Haines, chairman. Committee: A. H. Stover, G. R. Henry, K. G. Krech, J. Binswanger, J. B. Hill, and E. S. Esposito.



TABLE III. REFRACTIVE INDICES AT 20° C.						
(Figure at the left of decimal omitted)						
Commercial C	4437	4434	4434	4440	4436	4422
Synthetic C	4391	4392	4392	4397	4398	4387
Commercial D	4084	4080	4078	4077	4082	4068
Synthetic D	4023	4020	4018	4022	4026	4008
Commercial F	4695	4695	4696	4683	4699	4689
Synthetic F	4652	4660	4658	4658	4659	4650
Refractive Indices of Raffinate at 20° C.						
Commercial C	4113	4112	4115	4121	4121	4112
Synthetic C	4034	4049	4053	4070	4057	4048
Commercial D	3984	3998	4000	3997	4004	3979
Synthetic D	3925	3920	3925	3932	3933	3922
Commercial F	4134	4128	4121	4120	4124	4121
Synthetic F	4082	4056	4048	4074	4056	4058
Average Boiling Point						
° C./° F.						
Commercial C	110.5/231		Commercial F	110.5/231		
Synthetic C	101.5/215		Synthetic F	105.5/222		
Commercial D	108.3/227					
Synthetic D	98.9/210					

Table II shows that the present cooperators concord reasonably well in the compositions of the two commercial high-solvency type naphthas, as well as in the compositions of their synthetic matches. Accuracy of the method, as it stands, is of the order of  $\pm 0.5$  per cent of the whole thinner in the aromaticity of the two commercial high-solvency naphthas; and aromaticity is considered the most important property of a high-solvency thinner. Baldeschwieler *et al.* (1, 2) have shown that, according to kauri-butanol values, an aromatic hydrocarbon, in the usual commercial boiling ranges, has approximately double the solvency of the corresponding naphthene, which in turn has nearly double the solvency of the paraffin.

On the other hand, both accuracy and precision are poor in the case of the single low-solvency naphtha, and work is now in progress to refine the method to deal with such materials.

These results in Table II are derived from the refractive indices and average boiling points given in Table III.

Considering the two high-solvency type naphthas C and F, whose aromaticities agree reasonably well with those of their corresponding synthetic matches, poor agreement is observed between the paraffinic and naphthenic contents of the commercial products and their synthetic matches. It is probable that a part of the discrepancy is due to the wide difference in the types of paraffins present: mixtures of highly branched paraffins

in the high-solvency commercial naphthas *vs.* *n*-heptane alone in the synthetic blends.

A further estimate of the accuracy of the proximate analytical method, as it stands, is a comparison of the viscosities of solutions in each pair of commercial and synthetic thinners of resins and a standard nitrocellulose solution. In addition, the comparative kauri-butanol values, mixed aniline points, and refractive indices serve as accuracy indications. Table IV lists these various comparisons. Each cooperator used the same alkyl resin, modified phenolic and 37.5 per cent solution of 0.5-second nitrocellulose (containing 20 per cent ethanol) in *n*-butyl acetate. Kauri-butanol solutions, however, were of dissimilar strengths; and two cooperators substituted the mixed aniline point test for the kauri-butanol determination. Mixed aniline point is the critical solution temperature of a mixture of 5 cc. of thinner, 5 cc. of any

FIGURE 1. COMPOSITION-BOILING POINT-REFRACTIVE INDEX CHART FOR AROMATIC-FREE NAPHTHA

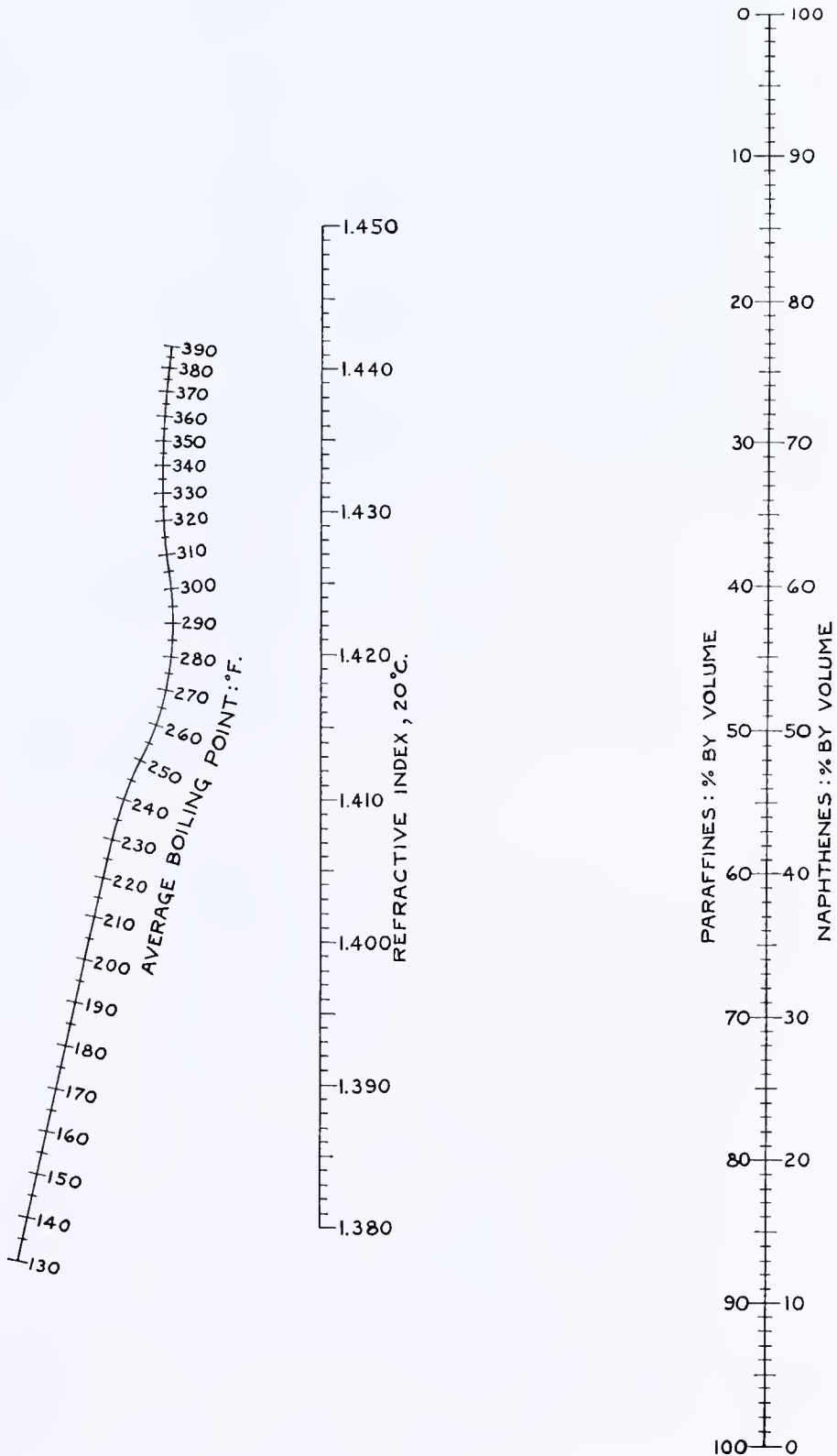




TABLE IV. COMPARATIVE VISCOSITIES<sup>a</sup>

Thinner	(Cooperators 1 to 6)					
	1	2	3	4	5	6
50% Solution of Modified Phenolic Resin						
Commercial C	F+	E	E+ $\frac{1}{2}$	E+	F	E+
Synthetic C	F-	D	C+ $\frac{1}{2}$	E	D	E
Commercial D	..	T+2B	..	U	X	..
Synthetic D	..	T+3B	..	U	X+	..
Commercial F	C	D+	C	C+	B+	C
Synthetic F	B	C-	B+ $\frac{1}{2}$ B	C-	C	B/C
60% Solution of Alkyd Resin						
Commercial C	D+	F	E	F- $\frac{1}{2}$ B	..	E
Synthetic C	D	F-	E- $\frac{1}{2}$ B	E- $\frac{1}{2}$ B	..	E
Commercial D	M	N	K- $\frac{1}{2}$ B	L	..	K
Synthetic D	L	H	K	J	..	J
Commercial F	B	C-	C	B+ $\frac{1}{2}$ B	..	B
Synthetic F	B	A	C	B+ $\frac{1}{2}$ B	..	C
37.5% 0.5-Second Nitrocellulose Solution Thinned 60/40 with Thinners						
Commercial C	X	X- $\frac{1}{2}$ B	X+ $\frac{1}{2}$ B	W-	X	W
Synthetic C	X+ $\frac{1}{2}$ B	X- $\frac{1}{2}$ B	X+ $\frac{1}{2}$ B	W-	X	W+ $\frac{1}{2}$ B
Commercial D	Y+ $\frac{1}{2}$ B	Y	Z+ $\frac{1}{2}$ B	..	X/Y	Y- $\frac{1}{2}$ B
Synthetic D	Y+ $\frac{1}{2}$ B	Y	Z+ $\frac{1}{2}$ B	..	X+ $\frac{1}{2}$ B	Y- $\frac{1}{2}$ B
Commercial F	W	W	W+ $\frac{1}{2}$ B	U/V	V	W- $\frac{1}{2}$ B
Synthetic F	W	W- $\frac{1}{2}$ B	W	U+	V- $\frac{1}{2}$ B	W- $\frac{1}{2}$ B
Kauri-Butanol Values (Cooperators 1 to 4) and Mixed Aniline Points in ° C. (Cooperators 5 and 6)						
Commercial C	61.9	60.6	56.4	59.6	40.5	39.4
Synthetic C	60.4	59.5	55.3	58.3	40.6	39.6
Commercial D	35.0	35.3	32.5	36.2	59.0	..
Synthetic D	34.1	33.4	31.1	34.9	59.0	..
Commercial F	84.2	83.2	79.1	80.2	24.6	25.0
Synthetic F	83.1	81.5	76.9	78.4	25.4	25.4

<sup>a</sup> "F+" indicates a viscosity heavier than tube F; "F+ $\frac{1}{2}$ B", one quarter bubble heavier than F; "F- $\frac{1}{2}$ B", one quarter lighter than F.

naphtha whose straight aniline point is 60° C., and 10 cc. of anhydrous aniline (4). Each cooperator's data should be considered *per se*, since the viscosity of a synthetic resin solution is affected not only by the heat treatment received during solution, but also by the time and method of agitation. Viscosities, expressed in terms of Gardner-Holdt bubble-tube letters, were determined with each cooperator's own set of standards.

In considering the comparative viscosities of resin solutions, the differences in average boiling points shown in Table III should be noted. The higher molecular weights indicated by the higher boiling ranges of the commercial solvents make for a higher molal resin concentration in a given resin solution made on a weight basis.

Conclusion

The refractive index-sulfuric acid extraction method for determining the aromaticity of commercial high-solvent hydrocarbon thinners, whose evaporation rates are similar to that of toluene and which are substantially olefin-free, provides results which are reasonably accurate, as shown by comparison with synthetic blends, and can be duplicated by several cooperating laboratories with a precision of  $\pm 0.5$  per cent. Although the method, as it stands, does not determine the naphthenic or paraffinic contents with the accuracy or precision which may be desired, the relatively greater importance of aromaticity is demonstrated by a reasonably good concordance in the viscosities of solutions of film-forming materials in the commercial thinners and their synthetic matches.

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# A Modified Beilstein Test for Halogens in Volatile Organic Compounds

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DURING an investigation of the low-boiling fraction obtained in the commercial production of divinyl ether, vinyl chloride was isolated. The need arose for a rapid sensitive test to detect this impurity in the finished product.

The well-known Beilstein test (1) for detecting halogens in organic compounds, either with copper oxide in a platinum loop or with plain copper wire, is inapplicable to highly volatile substances and in order to detect vinyl chloride (b. p. -13.9° C.) in divinyl ether (b. p. 28.3° C.) the following modification was developed.

A piece of clean copper screen 10 cm. square, with about 8 meshes to the inch of fairly heavy wire, is clamped 4 cm. above an ordinary Bunsen burner. The flame is allowed to burn on both sides of the gauze until all trace of green color disappears. The liquid to be tested for halogen is then added drop by drop from a separatory funnel to a warmed 125-cc. flask through which the gas supply to the burner passes. The presence of halogens is evidenced by the appearance of a green color in the flame.

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With careful observation in a darkened room the limit sensitivity was found to be 0.005 per cent of vinyl chloride which corresponds to about 30 parts per million of chlorine. Under the same conditions 0.025 per cent of vinyl chloride gave a strong green flame.

Since this paper was submitted, Stenger, Shrader, and Beshgetoor (2) have described a modified Beilstein test which is ideally adapted to the detection of volatile halogen compounds in the air, particularly under the conditions found when leak appear in refrigerator pumping systems. The author's modification, which was completed in March, 1934, was designed primarily for laboratory use to determine halogens in volatile liquids, but it could also be used to determine halogens in samples of a gas or air. The sensitivity of both tests is of the same order of magnitude.

Literature Cited

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# Separation and Determination of Copper and Nickel by Salicylaldoxime

## Effect of Hydrogen-Ion Concentration

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EPHRAIM (3) developed a method for the gravimetric determination of copper by the use of salicylaldoxime as precipitant. The procedure had to be modified for the analysis of mixtures containing iron because the complex formed by this metal with the reagent is entrained from solution by the copper precipitate (4, 12). Salicylaldoxime has also been employed for the analysis of copper-cadmium mixtures (7) and for the determination of lead (8), nickel (13), zinc (11), and palladium (5). Chambers (2) has reported its use for the simple and rapid determination of copper and nickel in various alloys.

The hydrogen-ion concentration range of the solution from which various metal salicylaldoxime complexes can be separated quantitatively is limited by the composition of the mixture. Riley (13) recommends the analytical precipitation of nickel from a solution which is just acid. Pearson (11) states that nickel must be separated from mixtures containing zinc and low concentrations of ammonium salts at a pH of exactly 6.5. The zinc complex starts to precipitate at a pH just above this value if the salt concentration is too low to keep it in solution. Workers for Hopkin and Williams, Ltd. (6) state that the pH should be 7 to 8 to ensure complete precipitation of nickel. Chambers (2) separates the nickel complex from an alkaline solution.

During an investigation of entrainment of various substances from solution by insoluble metal salicylaldoxime complexes, it was necessary to study the effect of varying the hydrogen-ion concentration on the separation and determination of copper and nickel by means of the reagent. Analyses were made on solutions of the pure salts to determine the pH range in which the results were quantitative. The method was then applied to mixtures of the salts to find the limits of hydrogen-ion concentration between which the metals could be completely separated.

The entrainment of the nickel complex by the copper precipitate was investigated at both fixed and varying hydrogen-ion concentration. Similar studies were carried out on iron entrainment.

Standard samples of alloys containing comparatively large and small amounts of copper were analyzed. Salicylaldoxime reagent was used for separation and determination of the copper.

### Solutions

Nickel, 99.93 per cent pure, containing no iron or copper, was obtained from the International Nickel Company. After dissolving the metal in redistilled nitric acid, the solution was diluted to contain 1 gram of nickel per liter. The concentration of the standard solution was checked by determinations with methylglyoxime and subsequently with salicylaldoxime. Standard copper solutions were made up from thrice recrystallized Mallinckrodt analytical reagent copper sulfate and from electrolytic copper dissolved in redistilled nitric acid. The solutions contained approximately 1 gram of copper per liter. The copper concentration was found by electrodeposition and volumetric titration, later checked by salicylaldoxime determinations.

Standard iron solutions were prepared from Baker primary standard iron wire, 99.8 per cent pure, which was dissolved in Mallinckrodt analytical reagent hydrochloric acid and diluted to concentration of 1 gram per liter.

A 1 per cent solution of salicylaldoxime was used for all separations and determinations. The reagent was prepared according to Ephraim (3), by adding, without stirring, a solution of 1 gram of salicylaldoxime in 5 ml. of 95 per cent alcohol to 95 ml. of water heated to 80° C. The solution was cooled, stirred, and filtered. The reagent was also prepared by the method of Astin and Riley (1), by adding 2.22 grams of salicylaldehyde dissolved in 8 ml. of 95 per cent alcohol to 1.27 gram of hydroxylamine hydrochloride dissolved in 2 ml. of water. The resulting solution was diluted with 15 ml. of 95 per cent alcohol and stirred into 225 ml. of water at 80° C. The reagent was filtered before use.

As the salicylaldoxime slowly decomposes in solution and the decomposition products are removed with difficulty, no reagent more than 3 days old was employed.

The salicylaldoxime, salicylaldehyde, and hydroxylamine hydrochloride used to prepare the reagent solutions were the "highest purity" grade obtained from the Eastman Kodak Company. The glacial acetic acid, ferric chloride, and sodium acetate reagents were Mallinckrodt analytical reagent quality. Solutions of sodium hydroxide and ammonia were prepared from Baker C. P. chemicals.

All volumetric ware employed was carefully calibrated. Adjusted weights were used.

### Hydrogen-Ion Concentration

All measurements of hydrogen-ion concentration were carried out by use of a glass electrode pH meter (9), calibrated by Clark and Lubs buffer solutions which had been standardized against a hydrogen electrode.

Whenever possible, preliminary adjustment of acidity was carried out before the addition of the reagent. If it was desired to adjust the pH of the solution to a definite value, the readings were taken on the supernatant liquid and the hydrogen-ion concentration was regulated while the precipitate was still in contact with the mother liquor. The mixtures were then vigorously stirred for some time and allowed to stand for several hours, usually overnight. Because of the change in hydrogen-ion concentration caused by the addition of the reagent solution and the precipitation reaction, all final recorded values of pH were obtained by measurement on the filtrate collected before washing the precipitate.

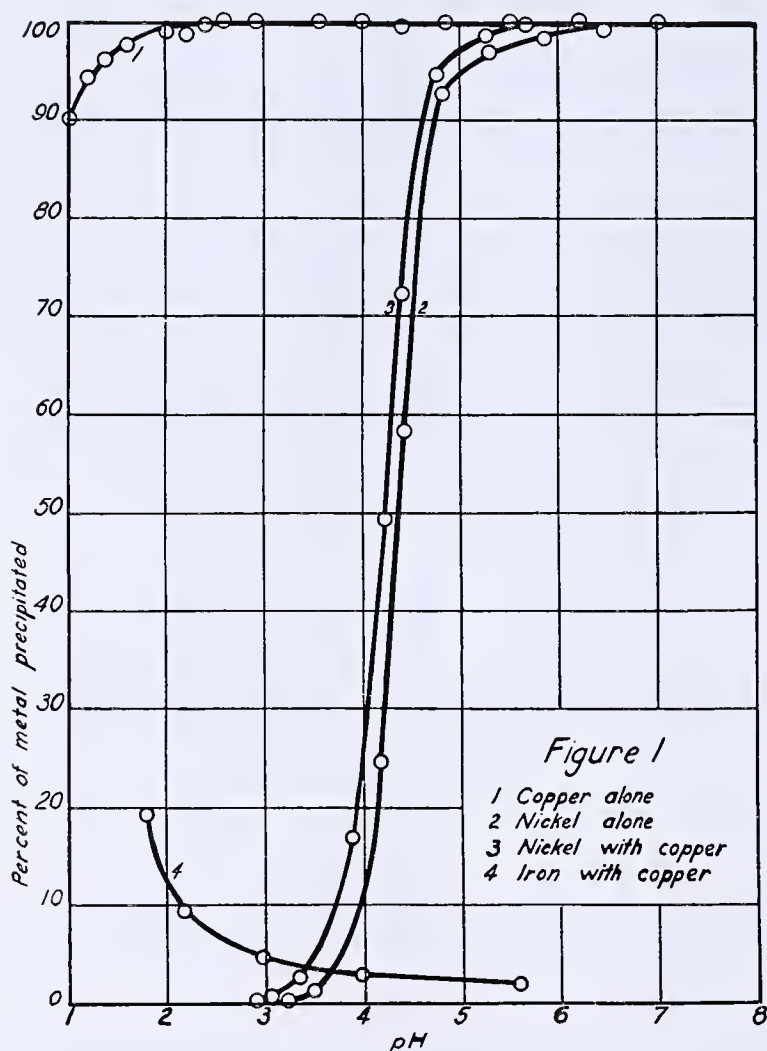
The use of a universal indicator for carrying out preliminary acidity adjustment was tried, but a slight coloration of the solution itself necessitated such a high concentration of indicator that it precipitated in the aqueous solution and caused high results to be obtained. Litmus paper was found useful for preliminary adjustment of acidity before precipitating the nickel complex.

### Procedure

**COPPER.** The desired volume of copper standard solution was diluted to about 100 ml. in a 250-ml. beaker. Filtered 2 *N* sodium hydroxide was added dropwise, with vigorous stirring, until a permanent precipitate of the basic copper salt formed; then 0.5 ml. of the base was added in excess, to provide for any irregularity in the acidity of the mixture. The precipitate was dissolved in the least amount of glacial acetic acid. (The acidity of the solution at this point is correct for the quantitative precipitation of the copper salicylaldoxime complex.) Variation in hydrogen-ion concentration was next obtained by adding varying amounts of glacial acetic acid or sodium hydroxide solution. The quantity of acid or base to add was determined by pH measurements on the solution.



The salicylaldoxime reagent, in 50 per cent excess, was added dropwise from a buret while the solution was mechanically stirred. The mixture was allowed to stand several hours, usually overnight, and then the precipitated copper complex was washed by decantation, and filtered by aid of suction through a glazed porcelain porous-bottom "Berlin" A2 filtering crucible. The precipitate was washed with cold water until the filtrate gave no coloration on the addition of ferric chloride solution. The complex was kept moist until the final washing, after which it was sucked dry, heated for 1 hour in an electric oven at 100° C., and weighed as  $\text{Cu}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ . The pH of the filtrate, washings not included, was measured by use of a glass electrode.



If copper is originally present as the nitrate rather than as the sulfate, the precipitate of the salicylaldoxime complex adheres less to the glass.

**NICKEL.** Analyses of standard solutions containing nickel were carried out in a manner similar to those on copper solutions. The acidity was adjusted with varying amounts of ammonia and sodium acetate. The salicylaldoxime reagent was then added dropwise while the solution was vigorously stirred. The precipitate was suction-filtered, washed, dried for 1 hour at 100° C., and weighed as  $\text{Ni}(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$ . The pH of the filtrate was measured.

**COPPER AND NICKEL MIXTURES.** Separations of copper from nickel were performed by adding the salicylaldoxime reagent in an amount sufficient to provide an excess over the theoretical quantity needed for the precipitation of both metals. The copper complex was precipitated from an acid solution. A dilute ammonia solution was added dropwise, with stirring, to the combined filtrate and washings from the copper precipitate until the mixture had the desired hydrogen-ion concentration. It was stirred vigorously for about an hour and allowed to stand overnight. The resulting insoluble nickel complex was separated and determined according to the procedure outlined above. The pH of the filtrate, before the washings were collected, was determined each time. The extent of entrainment of the nickel with the copper complex was determined at a pH of 3.1 by precipitating the metals from mixtures of standard solutions. Each mixture contained 25 mg. of copper but varying amounts of nickel.

The variation of entrainment with hydrogen-ion concentration was measured for mixtures containing 25 mg. of each metal. The weight of the precipitate obtained from the mixture minus the theoretical weight of the copper complex present was compared to the weight of the precipitate obtained from a pure nickel solution of the same concentration, at the same pH value, and under similar experimental conditions.

**COPPER AND IRON MIXTURES.** A series of solutions containing different concentrations of iron and 25 mg. of copper was prepared. The copper was precipitated from each mixture at a pH value of 2.8. The difference between the weight of the precipitate and the theoretical weight of the copper complex present gave the amount of iron complex entrained. Similar measurements were carried out with mixtures containing 25 mg. of each metal, but the copper was precipitated at different hydrogen-ion concentrations.

**STANDARD ALLOY SAMPLES.** The procedure for the determination of copper in standard solutions was applied to the analysis of two National Bureau of Standards analyzed alloy samples, Nos. 37 and 95. The former contained 70.29 per cent of copper, the latter 2.87 per cent. Additional metals present were zinc, magnesium, lead, tin, and iron. Approximately 0.25-gram portions were dissolved in dilute nitric acid and diluted to about 100 ml. The copper salicylaldoxime complex was precipitated from a solution having a pH of 2.8, measured on the filtrate. Zinc and lead do not precipitate at this pH. Since less than 1 per cent of iron was present in each alloy, it did not interfere. Treatment with tartaric acid (12) or sodium carbonate (4) was unnecessary. The aliquot part method of measurement was used for the sample containing a large amount of copper in order to reduce errors due to weighing a small sample and to provide a precipitate of convenient weight.

## Results and Discussion

At first, analyses of standard copper solutions did not yield reproducible results. The difficulty was due to the high concentration of hydrogen ions introduced by the reagent and by the precipitation reaction. The reagent prepared according to Astin and Riley (1) has a pH of about 1.3. As this solution is added to precipitate the copper complex, the pH of the mixture gradually decreases. If the pH value becomes low enough, the separation of the copper is no longer complete. To counteract this increase of hydrogen ions occurring during precipitation about 0.5 ml. excess of 2 M sodium hydroxide was added previous to the addition of the salicylaldoxime reagent.

The results of the various studies are shown graphically in Figures 1 and 2. All analyses were run in triplicate.

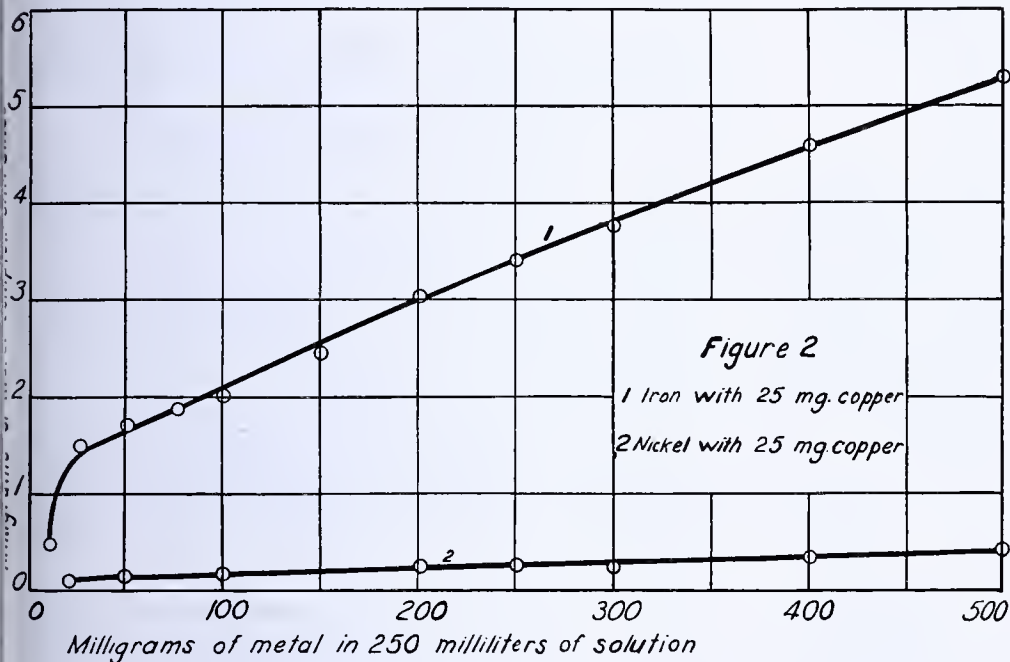
The determinations of copper in pure solutions at varying hydrogen-ion concentrations are summarized in Figure 1, curve 1. Each solution contained approximately 25 mg. of the metal. The percentage of copper precipitated is plotted against the pH value of the resulting filtrate. The curve shows that the lower pH limit for the quantitative precipitation of the copper salicylaldoxime complex from solution containing no other metal, except sodium, is 2.6. Figure 1, curve 2, represents the results of similar determinations on nickel in pure solutions at varying pH values. As indicated by the curve, the nickel complex starts to precipitate at a pH of 3.3.

From the results of analyses of pure solutions, the pH range for the analytical separation of copper from nickel would be predicted as 2.6 to 3.3. Figure 1, curve 3, gives the experimental results of separation of copper from nickel in solutions having different pH values. The curve is parallel to curve 2 and shifted over about 0.2 pH unit. This means that the amount of nickel precipitating out at a certain pH is about the same as would precipitate from a pure nickel solution at the same pH. The presence of the copper complex precipitate has very little effect on the solubility of the nickel complex. The actual pH range for the separation of copper from nickel is about the same as that predicted. The nickel complex does not start to coprecipitate with the copper complex until the solution has a pH of 3.1. This situation might be ex-



asted with that encountered in the use of 8-hydroxyquinone to separate certain metals (10).

As shown by Figure 1, curve 2, the quantitative precipitation of nickel started at a pH of 7.0. Determinations of the metal in solutions having a pH value as high as 9.9 gave satisfactory results, but those having a pH value less than 10 gave low results. Perhaps the presence of other salts affects the solubility of the nickel complex as is the case with zinc (11). This might explain the findings of Riley (13), precipitation of nickel from an acid solution, and of Pearson (1), precipitation of nickel from a solution at a pH of exactly 5. The salt effect will be investigated in connection with entrainment studies.



Examination of Figure 2, curve 2, shows that very little entrainment of nickel by the copper complex occurs at a pH value of 3.1, even if the nickel concentration is twenty times that of copper. The curve gives the results of copper separations carried out at a hydrogen-ion concentration just under the value at which the nickel complex starts to precipitate from a pure solution (see curve 2, Figure 1). The mixtures used contained about 25 mg. of copper and varying amounts of nickel.

Figure 2, curve 1, represents the entrainment of the iron complex precipitated from solutions whose pH values were 8. This value was chosen for the study because copper is completely precipitated and the entrainment of iron is fairly high. The ratio of the iron concentration to copper was increased to 20 to 1. Over the range of concentrations investigated, the plotted entrainment values do not give the adsorption isotherm type of curve. The probable conclusion is that the carrying down of the iron complex is not due to adsorption alone. Figure 1, curve 4, shows the results of precipitation of about 25 mg. of copper in the presence of 5 mg. of iron at varying pH values. The entrainment of the iron complex by the copper increases with increasing hydrogen-ion concentration of the solution. Results are not shown for pH values higher than about 5 because here the basic precipitate of iron starts to precipitate.

As pointed out by other workers, salicylaldoxime is an excellent and fairly sensitive reagent for copper; under suitable conditions it is specific. Analyses for copper in standard samples of alloys were carried on easily and rapidly. The sample containing 70.29 per cent of copper yielded an average of 70.32 per cent; that containing 2.87 per cent gave

2.85 per cent. The separation and determination of copper, in triplicate, took about 2 hours. The precipitate of the copper complex is easy to handle, no digestion is required, and the residue is weighed without further treatment after drying.

The best quantity of sample to take for analysis is that which will yield a precipitate weighing from 50 to 300 mg. Smaller samples tend to introduce weighing errors, whereas larger ones excessively lengthen time of manipulation.

It is interesting to compare dimethylglyoxime with salicylaldoxime as a reagent for nickel. Determinations of nickel in various mixtures by the use of either reagent yield results of about the same precision and accuracy. Perhaps

the former is more specific for the metal, but the latter forms a precipitate which is easier to handle. If certain interfering constituents, such as iron, are not present in high concentration, the salicylaldoxime method is more rapid. The cost of the reagent is not excessive, if made by the simple addition of salicylaldehyde to hydroxylamine hydrochloride (1), whereas many analytical organic reagents are not practical because of their present cost.

### Summary

Hydrogen-ion concentration is an important factor in the use of salicylaldoxime as an analytical reagent.

Copper salicylaldoxime complex starts to precipitate from pure solutions in quantitative amounts at a pH of 2.6. Nickel salicylaldoxime complex starts to precipitate from

pure solutions at a pH of 3.3. The amount is quantitative at a pH of 7.0. The pH range of separation of copper from nickel by the use of the reagent is 2.6 to 3.1. This range is not appreciably different from that predicted by results obtained with pure solutions.

Very little entrainment of the nickel complex by the copper complex was found. The presence of the copper precipitate does not appreciably affect the solubility of the nickel complex. Entrainment of the iron complex occurs over the entire range of hydrogen-ion concentration studied. It is not due to adsorption alone. The amount decreases with increase of pH.

Salicylaldoxime affords a rapid, simple, accurate, and fairly cheap method for the separation and determination of copper and nickel in various mixtures.

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# Determination of Iron in Tungsten and Tungstic Acid

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The small amounts of iron in tungsten metal and in tungstic acid have been determined by a method which involves an electrolytic separation of the iron from the bulk of the tungsten as a tungsten-iron alloy, the precipitation of the iron in the alloy as ferric hydroxide, and its quantitative determination by the iodometric method.

A VERY small percentage of iron present as an impurity in metallic tungsten has a marked effect on the physical properties of the metal—for example, iron decreases the grain size in a sintered tungsten bar and also tends to make the metal brittle. Tungsten containing 0.1 per cent of iron is practically unworkable (5), and standard grades of tungsten usually contain only a small amount of iron, in the neighborhood of 0.005 per cent and not exceeding 0.01 per cent (1). Thus a new method for the quantitative determination of the iron impurities present in tungsten and tungstic acid ( $\text{H}_2\text{WO}_4$  or the anhydride,  $\text{WO}_3$ ) should have a definite value.

The main difficulty in determining the iron in tungsten is to get a complete separation of the small amounts of iron. In the usual procedure the iron is precipitated as ferric hydroxide by sodium hydroxide, which leaves the tungsten in solution as sodium tungstate. However, a soluble tungstate-iron complex may form and thus leave appreciable amounts of iron in solution. Recently Holt (4) found that a tungsten-iron alloy containing 15 to 35 per cent of iron, depending on conditions, can be electrodeposited from the aqueous alkaline tungsten plating bath suggested by Fink and Jones (2). It was shown that the amount of electrodeposited alloy depended primarily on the amount of iron impurity in the bath and that continued electrolysis removed all the iron from the plating solution. These facts suggested a new method for determining the iron in tungsten or tungstic acid: the preparation of a plating bath from the sample to be analyzed, the electrolytic separation of the iron impurities as a tungsten-iron alloy deposited on the cathode, and then a quantitative determination of the iron in the alloy.

## Materials and Electrolysis Procedure

**Sodium Carbonate Solution.** This solution contained about 300 grams of reagent quality anhydrous sodium carbonate per liter. The solution was allowed to stand about 12 hours, then warmed and filtered through special filter paper.

**Sodium Hydroxide Solution.** This solution was prepared as used from a saturated solution of reagent sodium hydroxide.

**Standard Iron Solution.** Pure iron wire was dissolved in hydrochloric acid with a little nitric acid and made up to the required volume. One milliliter contained 1 mg. of iron.

**Purified Tungstic Acid.** Barium tungstate was precipitated from sodium tungstate solution and digested with hydrochloric-nitric acid to give tungstic acid; this was dissolved in ammonium hydroxide and the solution filtered. Tungstic acid was then reprecipitated with hydrochloric-nitric acid, washed by decantation, and carefully dried.

**Sodium Thiosulfate Solution.** A dilute solution (approximately 0.005 *N*) was prepared from a 0.1 *N* solution to which a very small amount of sodium bicarbonate had been added. It was standardized with sodium iodate for each series of titrations.

**Starch Indicator.** This solution was prepared from soluble starch as needed.

**Buret.** A 5-ml. microburet, graduated to 0.02 ml., was used for all titrations.

**Method of Electrolysis.** Pyrex beakers (100-ml.) served as plating cells. Anodes were of platinum  $3 \times 3$  cm. The cathode of electrolytic copper foil,  $3 \times 3$  cm., was so arranged as to be easily detached from a platinum cathode lead. A cathode current density of 10 to 20 amperes per sq. dm. from a generator through a lamp-bank or from a copper oxide rectifier, was employed. A plating run was timed to about 25 minutes and a new copper foil cathode was always used for each run. The plating bath temperature was kept at about 90° C. Two cells connected in series made it possible to carry out runs in duplicate when seemed advisable.

## Iron by the Iodometric Method

For reasons of simplicity and convenience the iodometric method was selected for the quantitative determination of the separated ferric hydroxide.

The ferric hydroxide, precipitated with ammonium hydroxide, was washed and then dissolved in about 9 ml. of approximately 4 *N* hydrochloric acid. It was carefully washed into a 125-ml. Erlenmeyer flask to give a total volume of about 60 ml. Then about 1 gram of solid sodium bicarbonate was added to the solution and the flask was stoppered with a cork having a small vent or outlet slit. The solution was warmed to about 50° C. and then 0.3 gram of potassium iodide (1 ml. of 30 per cent potassium iodide solution) was added. After about 5 minutes the liberated iodine was titrated with sodium thiosulfate solution. The starch indicator was added as the end point was approached as evidenced by the fading of the color of the solution.

Grey (3) reports that 0.05 mg. of iron can be accurately determined by this method and the authors found that known solutions of iron could be determined to within 0.02 mg. The use of an inert atmosphere such as carbon dioxide during the titration was found to be very important, although Grey (3) reports that reoxidation of  $\text{Fe}^{++}$  by air is negligible and that conditions to avoid this are superfluous. The authors found that known iron solutions gave consistent high results when titrations were carried out in the air.

TABLE I. ELECTROLYTIC SEPARATION OF IRON

Iron Added Mg.	Iron Found Mg.
2.0	1.98
2.0	1.97
2.0	1.99
1.0	1.02
1.0	0.99
0.5	0.54
0.5	0.53
0.2	0.20
0.2	0.21
0.05	0.06
0.05	0.07

## Purified Tungstic Acid and Added Iron

In order to check the completeness of the separation of iron from tungstic acid, known amounts of standard iron solution were added to a purified tungstic acid plating bath and then separated by electrodeposition as tungsten-iron alloy.

The plating bath was prepared by dissolving 8 grams of tungstic acid in 75 ml. of the sodium carbonate solution. This was electrolyzed once to ensure complete removal of the last traces of iron, then the known amount of iron was added while the solution was being stirred. Small amounts of added iron do not precipitate as the hydroxide from this alkaline plating bath, presumably because of complex formation. The iron was titrated



TABLE II. IRON IN TUNGSTIC ACID			
Brand of H <sub>2</sub> WO <sub>4</sub>	Trial	Iron Found	
		NaOH method %	Electrolytic method %
A	1	0.0045	0.0047
	2	0.0043	0.0050
	3	0.0045	0.0048
B	1	0.0009	0.0023 <sup>a</sup>
	2	0.0007	0.0025 <sup>a</sup>
	3	0.0008	0.0023 <sup>a</sup>
C	1	0.0011	0.0016
	2	0.0009	0.0015 <sup>a</sup>
	3	0.0009	0.0017 <sup>a</sup>
D	1	0.0041	0.0046
	2	0.0043	0.0047
	3	0.0041	0.0047
E	1	0.0011	0.0014 <sup>a</sup>
	2	0.0011	0.0014 <sup>a</sup>
	3	0.0010	.....
F	1	0.0057	0.0066
	2	0.0060	0.0069
	3	0.0058	0.0070

<sup>a</sup> 20-gram sample.

removed from the hot bath as tungsten-iron alloy by 3 or 4 successive plating runs. A thin alloy film on the copper cathode seems to interfere with continued deposition on that cathode, so successive runs with new copper cathodes are necessary to remove all the iron. That the iron was completely removed from the bath by such a procedure was proved by an additional plating run with a new copper cathode. No cathode deposit was obtained then, but if as little as 0.05 mg. of iron was added to such a bath it gave on electrolysis a weighable cathode deposit and even smaller amounts of iron had a definite cathode effect. The copper cathodes plated with the small amount of tungsten-iron alloy were put in a 100-ml. beaker, covered with about 50 ml. of water, and then dissolved in 8 ml. of hydrochloric-tri- c acid. An additional 10 ml. of hydrochloric-nitric acid was then added and the solution was carefully evaporated to about 10 ml. to ensure fairly complete precipitation of the tungsten as tungstic acid and then diluted before filtration. The iron was precipitated from the filtrate by ammonium hydroxide with gentle stirring and a short period of standing to ensure coagulation. Filtration, washing, redissolving, double precipitation, and careful washing removed all traces of copper. The iron was then determined by the iodometric method. Care was taken to remove all the copper, because according to Grey (3) even traces interfere with the method for determining iron. Separate runs showed that the ferric hydroxide was free of copper. Also the copper foil used gave negative tests for iron.

Typical results obtained on the analysis of a number of known solutions are given in Table I, and show that the electrolytic separation of known amounts of iron from the plating bath is very satisfactory.

Iron in Commercial Tungstic Acid

Six representative brands of technical and c. p. tungstic acid were chosen for analysis. To check the value of this new method all samples were analyzed by the usual sodium hydroxide separation and by the electrolytic separation. Ten-gram samples were used for analysis unless otherwise indicated and all per cents are calculated on the basis of iron in tungstic acid.

In the sodium hydroxide method the sample was dissolved in a sodium hydroxide solution which contained about 0.6 gram in excess of that required to form sodium tungstate, and then it was made up to a volume of about 125 ml. This was warmed to assist solution and to coagulate the ferric hydroxide. After standing about 12 hours it was filtered and the ferric hydroxide was washed, redissolved, reprecipitated, and then determined iodometrically. In the electrolytic method the sample was used to prepare a carbonate plating bath—10 grams of tungstic acid dissolved in about 90 ml. of the sodium carbonate solution. The bath was heated to about 90° C. and then electrolyzed in a series of 3 or 4 successive plating runs using new copper cathodes for each run. The small amount (1 to 6 mg.) of tungsten-iron alloy on the copper cathodes was then treated according to the procedure described for the known solutions.

Typical results showing the amounts of iron found by the two methods in various samples of tungstic acid are included in Table II.

In these analyses of tungstic acid the amount of iron found by the electrolytic separation was in all cases greater than that found by the sodium hydroxide method. This difference in the results supports the assumption that the formation of a soluble tungstate-iron complex may prevent the complete separation of iron from tungstic acid by sodium hydroxide. In similar later separations of iron with sodium hydroxide, the alkaline tungstate filtrate when used as a plating bath gave on electrolysis a weighable cathode deposit of iron-tungsten alloy.

TABLE III. IRON IN TUNGSTEN METAL				
Brand	Sample	Trial	Tungsten Used Grams	Iron Found %
I	A	1	2.9113	0.0162
		2	4.7646	0.0160
		3	2.4986	0.0164
	B	1	3.0813	0.0106
		2	3.6570	0.0073
		3	4.3806	0.0079
II	A	1	3.1553	0.0079
		2	2.6362	0.0076
		3	3.3400	0.0072
	B	1	4.9511	0.0047
		2	5.5951	0.0054
III	..	1	3.5296	0.0030
		2	3.7627	0.0032

Iron in Metallic Tungsten

The analysis of tungsten metal required a special procedure for putting the sample in solution. Tungsten dissolves readily in alkali when used as the anode during an electrolysis at moderate current densities (6), and the plating bath was thus prepared by using the tungsten (strip, rod, or wire) to be analyzed as the anode and copper foil as the cathode with the usual sodium carbonate solution as the electrolyte. With moderate current densities the tungsten dissolves according to its chemical equivalent ( $W^{VI}$ ) to give a clear solution. If the current density is too high the resulting bath contains small amounts of dark substance, presumably a lower oxide which dissolves readily to give a clear solution when the bath is heated. Weighing the anode before and after electrolysis gave the amount of tungsten in the solution—i. e., the size of the sample to be analyzed. The iron was then separated from the bath as tungsten-iron alloy by 3 or 4 regular plating runs using platinum anodes and copper foil cathodes, the first of which was the cathode used during the anodic solution of the tungsten. The tungsten-iron alloy was analyzed by the usual method. Results of a number of analyses are given in Table III.

These results are not entirely satisfactory, but the lack of uniformity in the distribution of the iron throughout the samples may explain this variation. This is supported by the fact that excellent results were obtained when tungsten

TABLE IV. IRON IN POWDERED TUNGSTEN METAL			
Trial	0.0038 N Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Required ml.	Iron Found %	Variation from Average %
1	1.06	0.0045 (2)	+0.00010
2	1.03	0.0043 (8)	-0.00004
3	1.04	0.0044 (2)	.....
4	1.03	0.0043 (8)	-0.00004
	Av. 1.04	0.0044 (2)	.....

powder was used. For analysis of the powder, 5-gram samples were first oxidized to tungsten trioxide by careful heating in the air and then dissolved in the sodium carbonate solution to give the usual plating bath. The iron was then removed electrolytically and the resulting alloy analyzed in the regular manner. The results of the analysis of a c. p. tungsten powder (5-gram samples) are given in Table IV.



### Conclusions

The data presented show that the electrolytic method described is entirely satisfactory for the determination of iron in tungstic acid and powdered tungsten metal. The method is new in that it offers a means of removing the iron completely from the bulk of the tungsten compound in the form of a tungsten-iron alloy, which on the average contains about 20 per cent of iron. Thus instead of having to make a difficult and perhaps incomplete chemical separation of a few thousandths per cent of iron, it is necessary only to analyze the small amount of alloy thus obtained.

Since the iron is finally separated as ferric hydroxide, other ordinary impurities of tungstic acid should not interfere. The results given indicate that iron in tungsten or tungstic acid can be determined to within about 0.02 mg. by this electrolytic separation. The iodometric method for the

quantitative determination of these small amounts of iron was found to be very good and was chosen because it is relatively simple and requires very little experience. However, it is the alloy separation of the iron which is the basis of the method and any other preferred procedure, volumetric or colorimetric, could be used for the final determination of the iron.

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## Determination of Carotene in Silage

### An Improved Method

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ALTHOUGH the old Willstätter-Stoll (13) method for the determination of carotene has been modified and improved in recent years, all modifications (2, 7, 9) depend upon pigment distribution between petroleum ether and alcohol (90 per cent methyl or 85 per cent ethyl) for the separation of carotene and xanthophylls. This procedure has not proved reliable when applied to silage. Kane and Wiseman (4) found spectrographic evidence for pigments other than carotene in the petroleum ether solution of A. I. V. (acid-treated) silage. Peterson *et al.* (5, 6) showed that the carotene content of some A. I. V. silages was higher than that of the forage used in their preparation, and suggested that this might be due to pigments developed in the silage. Other workers (3, 11) have also found abnormally high carotene values for A. I. V. silages.

Subsequently Quackenbush, Steenbock, and Peterson (8) found that the carotene fraction obtained from A. I. V. alfalfa silages by the petroleum ether-ethyl alcohol procedure contained three pigments other than carotene. These pigments were separated from carotene by the use of magnesium oxide chromatograms and were found to be biologically inactive. Since these pigments amounted to as much as 40 per cent of the so-called carotene, the figures for such silages obtained by the petroleum ether-alcohol procedure are obviously too high.

In an attempt to find a method, other than the tedious chromatographic procedure which would separate the pigments, several solvents were used in place of 85 per cent ethyl alcohol. As a check on the effectiveness of the solvent, the carotene and noncarotene contents of the fractions were carefully determined by chromatographic separation. Clausen and McCoord (1) had used diacetone for the separation of the carotenoid pigments in blood and this solvent proved satisfactory for the separation of those in silage. While absolute separation of pigments with such similar solubilities is probably impossible, nearly quantitative results were obtained.

### Procedure

A 500- to 1000-gram sample of fresh silage is well mixed and ground. Twenty-five grams are weighed into a flask and 200 cc. of alcohol are added immediately. The mixture is refluxed for 40 minutes and the alcoholic solution decanted. The residue is extracted again by refluxing 40 minutes with another 200-cc. portion of alcohol and the solution decanted. To the combined alcoholic extracts 40 cc. of 20 per cent alcoholic potassium hydroxide are added, and the solution is shaken and allowed to stand overnight.

An alternative procedure to the alcohol extraction is to reflux the sample with alcoholic potassium hydroxide. The determination may then be run immediately. In either case the total volume of the alcoholic extracts must be measured as a basis for the calculation of the carotene content.

To remove any carotene not extracted by the alcohol 80 cc. of Skellysolve Benzine, b. p. 65° to 75°, are added to the residue and heated just to the boiling point. The flask is then set aside to cool.

Aliquots equivalent to equal amounts of silage are taken from both the supernatant Skellysolve and the alcoholic extract. Usually 5 cc. of the Skellysolve extract are placed in a separatory funnel with 2 cc. of 20 per cent alcoholic potassium hydroxide and shaken. Twenty-five cubic centimeters of the alcoholic extract are then added, followed by 15 cc. of Skellysolve and or 8 cc. of water, and the mixture is well shaken. After complete separation of the two layers, the alcoholic solution is drawn off and re-extracted with two more 15-cc. portions of Skellysolve. Three extractions are sufficient to remove all the carotene although the Skellysolve is still yellow with xanthophylls.

The combined Skellysolve extracts in a separatory funnel are washed free of alkali with four 15-cc. portions of water. The noncarotene pigments are then removed by extracting the Skellysolve solution with four 10-cc. portions of a diacetone solution consisting of 100 volumes of diacetone (acetone-free from Commercial Solvents Corp., Terra Haute, Ind.) and 10 volumes of water. The mixture is shaken vigorously after each addition of diacetone solution, and, after standing until complete separation of the phases, the lower layer is drawn off and discarded.

The carotene solution is now washed twice with water to remove diacetone, made to 50-cc. volume, and read upon the spectrophotometer.



TABLE I. LOSSES IN MAGNESIUM OXIDE CHROMATOGRAM

Sample	Hypophasic Solvent	Pigments Separated			Recovery %
		Apparent Carotene Mg./kg.	Carotene Mg./kg.	Noncarotene as carotene Mg./kg.	
Grass silage	85% EtOH	718	338	77	58
	Diacetone	678	493	36	78
A. I. V. alfalfa silage	85% EtOH	215	117	36	85
	Diacetone	168	132	11	84
Molasses alfalfa silage	85% EtOH	181	118	55	95
	Diacetone	138	109	3	81
Green alfalfa	85% EtOH	201	161	10	85
	Diacetone	196	160	5	84

Comparison with Other Methods

This procedure and a similar one using 85 per cent ethyl alcohol or 90 per cent methyl alcohol to remove the hypophasic pigments were compared upon numerous samples. To eliminate sampling errors equal aliquots of the original extracts from one sample of forage were taken. The value obtained by reading the final Skellysolve solution in the spectrophotometer has been designated "apparent carotene" in the tables, since this solution may contain considerable amounts of other pigments. If a quantitative separation is obtained, this is the actual carotene content. Both the hypophasic and epiphasic solutions were subjected to chromatographic analysis to determine the efficiency of the

procedure in removing the noncarotene pigments, and also to determine the amount of carotene removed by the hypophasic solvent. The Skellysolve solutions were washed three times with water to remove any diacetone, filtered through a little anhydrous sodium sulfate, and taken to dryness under reduced pressure. The pigments were then taken up in a small amount of Skellysolve and forced through the chromatogram with pressure. The columns were developed with Skellysolve, followed by Skellysolve containing small amounts of absolute alcohol as described by Quackenbush *et al.* (8). The pigments in the hypophasic solution were first transferred to Skellysolve by dilution of the solution with water and extraction with Skellysolve, and then treated in a similar manner. The fractions collected from the column were diluted to proper volume with Skellysolve and read in the spectrophotometer. Both the carotene and noncarotene pigments are reported in terms of carotene based upon  $E_{480}^{1\%} = 2150$  which was determined with pure  $\beta$ -carotene.

Results and Discussion

Since Quackenbush *et al.* (8) had shown that magnesium oxide columns give satisfactory separation of the pigments, this adsorbent was tried. Recovery from these columns, however, was neither quantitative nor consistent. In Table I

TABLE II. COMPARISON OF DIACETONE AND ALCOHOL METHODS

Sample No.	Forage	Hypophasic Solvent	Apparent Carotene Mg./kg.	Pigments Separated			Carotene in Hypophasic Solvent Mg./kg.
				Carotene Mg./kg.	Non-carotene Mg./kg.	Recovery %	
1	A. I. V. alfalfa silage	85% EtOH	285	195	45	84	..
		Diacetone	252	224	22	98	
2	A. I. V. alfalfa silage	85% EtOH	264	176	64	91	..
		Diacetone	248	192	24	87	
3	A. I. V. alfalfa silage	85% EtOH	332	250	70	96	..
		Diacetone	281	244	29	97	
4	A. I. V. alfalfa silage	85% EtOH	322	248	45	91	..
		Diacetone	310	265	17	88	
5	A. I. V. alfalfa silage	85% EtOH	181	151	33	102	3
		Diacetone <sup>a</sup>	156	151	5	100	
6	A. I. V. grass silage	85% EtOH	435	371	52	97	3
		Diacetone <sup>a</sup>	382	364	12	98	
7	A. I. V. pea silage	85% EtOH	143	103	34	96	..
		90% MeOH	149	103	34	92	
		Diacetone	120	109	11	100	
8	Phosphoric acid alfalfa silage	85% EtOH	238	197	46	102	..
		Diacetone	208	197	12	100	
9	Phosphoric acid alfalfa silage	85% EtOH	246	205	36	98	..
		90% MeOH	276	205	41	89	
		Diacetone	217	205	5	97	
10	Molasses alfalfa silage	85% EtOH	140	114	21	96	..
		Diacetone	130	119	10	99	
11	Molasses alfalfa silage	85% EtOH	505	442	45	96	..
		Diacetone	460	352	18	80	
12	Molasses alfalfa silage	85% EtOH	244	206	33	98	..
		Diacetone	202	211	5	107	
13	Molasses alfalfa silage	85% EtOH	171	144	20	96	..
		90% MeOH	171	144	20	96	
		Diacetone	156	144	4	95	
14	Corn and soybean silage	85% EtOH	64	47	6	83	..
		Diacetone	52	47	0	90	
15	Corn silage	85% EtOH	189	134	32	88	..
		Diacetone	167	134	16	90	
16	Corn silage	85% EtOH	59	40	10	85	..
		Diacetone	52	47	4	98	
17	Untreated alfalfa silage	85% EtOH	58	47	11	98	..
		90% MeOH	61	47	11	95	
		Diacetone	46	47	0	107	
18	Green corn	85% EtOH	256	238	12	98	..
		Diacetone	243	238	0	98	

<sup>a</sup> Extracted with five 10-cc. portions of diacetone.



are shown a few typical results in which the recovery varied from 58 to 95 per cent. Similar losses with aluminum oxide columns have been reported by Willstaedt and With (12). The table does show, however, that the apparent carotene was higher when alcohol was used to remove the hypophasic pigments, and indicates that this difference was due to the higher content of noncarotene pigments in the solution.

Magnesium oxide was discarded and several new adsorbents were tried. Calcium carbonate proved satisfactory. The carotene could be washed out of the column with Skellysolve and then the noncarotene pigments could be removed with Skellysolve containing 10 per cent of absolute alcohol.

The results obtained with numerous samples are shown in Table II. The column headed "apparent carotene" represents, as before, the reading of the Skellysolve solution before chromatographic analysis. The next three columns give the actual carotene and noncarotene pigments separated from this solution and the percentage recovery from the calcium carbonate chromatogram. Column 8, "carotene in hypophasic solvent", gives the carotene found in the diacetone or alcoholic solution when subjected to chromatographic analysis.

While there are occasional losses during the manipulations, the results clearly indicate that the apparent carotene values obtained from silages when either 85 per cent ethyl or 90 per cent methyl alcohol is used are considerably too high. This error is the result of the pigments other than carotene which remain in the Skellysolve solution. When diacetone is used, the error is greatly reduced, the apparent carotene nearly equaling the actual carotene. The loss of carotene in the diacetone solution is no disadvantage and actually decreases the error of the determination. Since some noncarotene pigment remains in the carotene fraction, and an almost equal quantity of carotene is removed, these errors cancel each other. When this is considered, the apparent carotene is practically equal to the actual carotene content. A calculation of the errors illustrates this: In sample 8 the apparent carotene value obtained with alcohol is 238 and the actual carotene content 197. If we assume that about 3 mg. were extracted by the alcohol, the total carotene content was 200 and the percentage error =  $\frac{38}{200} \times 100 = 19$  per cent. In the case of diacetone the total carotene was  $197 + 12 = 209$ , which is equal to the apparent carotene figure.

Some of the inconsistencies in the data are due not only to losses during the manipulations, but also to the errors involved in reading the spectrophotometer. These have been discussed by Shrewsbury *et al.* (10) and in the authors' experience appear to be about  $\pm 3$  per cent. Since readings were necessary upon three or four fractions of each sample, the combined errors may in some cases account for high or low recoveries, and also for the difference between the total carotene obtained from one sample by the two methods.

A further advantage of the diacetone method is that four or five washings are sufficient to remove the interfering pigments. The results with alcohol may be improved by numerous washings, but the amount of pigment removed each time is very small and it is impossible to tell when the removal is complete. Carotene is also lost in the alcohol, and thus the results may be either high or low, depending upon the number of washings.

The recovery of known amounts of carotene which were added to the crude alcohol extracts is shown in Table III. These values are the apparent carotene values after washing with diacetone and show satisfactory recovery of the added carotene.

Quackenbush *et al.* (8) have shown that at least some of the interfering pigments are produced by the action of acid upon lutein. In Table IV are shown the results obtained by the

alcohol and diacetone methods upon a sample of phosphoric acid alfalfa silage which was analyzed before and after treatment with acid. Two 25-gram samples were taken and placed in alcohol. To one were added 2.7 cc. of a 2 *N* mixture of hydrochloric and sulfuric acids. After standing overnight the two samples were extracted as usual and analyzed by both procedures. The use of 85 per cent alcohol gave much larger errors after acid treatment, whereas the error was only about 3 per cent in both samples when diacetone was used.

TABLE III. RECOVERY OF ADDED CAROTENE

Sample	Carotene Added Micrograms	Carotene Found Micrograms	Carotene Calculated Micrograms	Accuracy %
A. I. V. alfalfa silage	0	139		
	93	237	232	102
A. I. V. alfalfa silage	0	109		
	60.5	177	170	104
Molasses alfalfa silage	0	77		
	60.5	135	137	98.5
Corn silage	0	21		
	60.5	79	81	97.7

TABLE IV. EFFECT OF TREATING SILAGE WITH ACID

Sample	Hypophasic Solvent	Apparent Carotene Mg./kg.	Pigments Separated Carotene Mg./kg.	Non-carotene Mg./kg.
Phosphoric acid silage				
Analyzed before	85% EtOH	198	164	29
adding acid	Diacetone	174	164	5
Analyzed after				
treatment with	85% EtOH	290	159	120
acid	Diacetone	174	169	5

## Summary

An improved method for determining the carotene content of silages is reported. The improvement consists of the use of a diacetone solution (100 volumes of diacetone, 6 volumes of water) in place of the usual 90 per cent methyl or 85 per cent ethyl alcohol for removal of the pigments other than carotene. The greater accuracy of the method was shown by the determination of the actual carotene contents by chromatographic technique.

## Acknowledgment

The authors are indebted to F. W. Quackenbush for suggesting the use of diacetone and for other suggestions in working out the method.

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# Bromide Content of Fruits and Vegetables

## Following Fumigation with Methyl Bromide

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THE use of methyl bromide as a fumigant for certain food-stuffs in order to control insect pests has increased markedly in the past two years, and gives promise in many types of fumigation procedures because of its effectiveness at moderate concentrations (2, 3, 4).

In order to study the effect of methyl bromide on food-stuffs intended for human consumption it was considered necessary to determine the amount taken up by the produce during fumigation and the rate of volatilization after completion of the fumigation.

The analytical method herein described for the determination of total bromides in vegetable products is based on the work of Baughman and Skinner (1). Modifications have been used as microchemical procedures in studying the bromide content of vegetable and animal products by Neufeld (6) and Yates (7).

The macroanalytical procedure here described requires 50- to 100-gram samples of the produce. Samples were taken in their usual state, and no correction is made for water content. The material being analyzed was covered with 1 per cent alcoholic potassium hydroxide solution, which serves to dissolve and hydrolyze the methyl bromide, converting the volatile bromide to potassium bromide. The treated sample wasashed three times at 500° C., being extracted with hot water between ashings.

Mackie (4) and McLaine and Munro (5) give the results of analyses of fruits and vegetables following methyl bromide fumigation, but present no details as to the methods of

analysis or the times of sampling after fumigation. Their results are in fair agreement with the findings of this investigation.

The following method of analysis has been used in determining the bromide content of a variety of foodstuffs up to 48 hours after fumigation with methyl bromide.

### Reagents Required

Alcoholic potassium hydroxide, 10 grams per liter of 95 per cent ethyl alcohol.

Dilute sulfuric acid, 2 to 6 *N*.

Stock sulfuric acid, 1400 cc. of water plus 650 cc. of concentrated sulfuric acid.

Chromic acid solution, 1600 cc. of water plus 200 grams of chromic anhydride and 600 cc. of concentrated sulfuric acid.

Potassium iodide solution, 100 grams of potassium iodide plus 1000 cc. of water (make fresh daily).

Standardized sodium thiosulfate solution, about 0.01 *N*.

Prepare above reagents and allow to come to room temperature.

### Procedure

Place a 50- or 100-gram sample of fruit or vegetable in a 10-cm. Pyrex or porcelain evaporating dish, cover with about 100 cc. of alcoholic potassium hydroxide, and allow to stand overnight at room temperature. Evaporate the alcohol and dry thoroughly on a low hot plate. Place the dish in a heated muffle furnace, ignite, and hold at 500° C. for 2 to 3 hours. Extract with two 50-cc. portions of hot water, filtering through No. 2 filter paper. The filtrate may be caught in a 400-cc. beaker. Remove the filter paper, add to dish, and dry dish and contents on a hot plate. Place the dish in a heated muffle furnace controlled at 500° C., ignite the paper, and heat until charcoal ceases to glow. Remove,

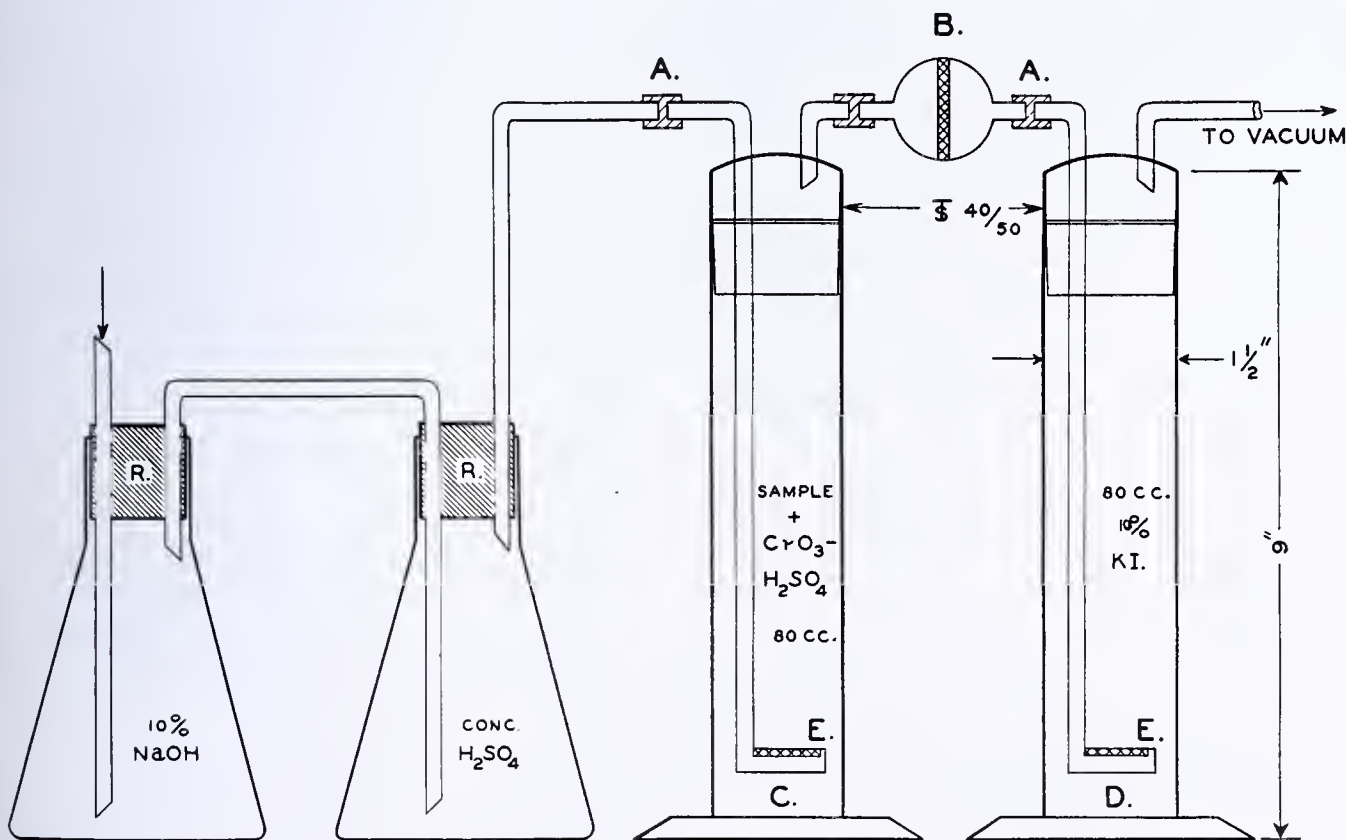


FIGURE 1. APPARATUS FOR ASPIRATING BROMINE

- A. All connections glass to glass, rubber sleeved  
B. Spray trap, sealed-in sintered-glass disk  
C, D. All-glass bubblers having sintered-glass foot, E, on bubbler stem.  
Air flow 500 to 800 cc. per minute



TABLE I. ACCURACY AND REPRODUCIBILITY OF RESULTS

Sample	Br Taken Mg.	Br Found in 5 Determinations			Average Recovery %
		Minimum Mg.	Maximum Mg.	Average Mg.	
KBr added directly to bubbler containing H <sub>2</sub> SO <sub>4</sub> -CrO <sub>3</sub> . Aspirated as shown in method <sup>a</sup>	1.48	1.47	1.50	1.48	100.0
	3.71	3.69	3.72	3.70	99.7
	7.41	7.38	7.43	7.41	100.0
KBr added to dish. Heated at 500° C. for 2 hours. Residue rinsed directly into bubbler with stock H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	1.48	1.02	1.18	1.12	75.7
	3.71	3.45	3.58	3.51	94.6
	7.41	7.22	7.49	7.34	99.0
KBr + 100 cc. of 1% alcoholic KOH. Taken through entire procedure <sup>a</sup>	1.48	0.93	1.08	1.02	68.9
	3.71	3.37	3.42	3.40	91.7
	7.41	7.25	7.56	7.45	100.5
KBr + 10 grams of charcoal + 100 cc. of 1% alcoholic KOH. Taken through entire procedure <sup>a</sup>	1.48	1.39	1.50	1.45	98.0
	3.71	3.59	3.78	3.71	100.0
	7.41	7.39	7.71	7.57	102.1
KBr added to 100 grams of potato pulp. Carried through entire procedure <sup>a</sup>	0	0.23	0.35	0.30	...
	1.78 <sup>b</sup>	1.65	1.75	1.71	96.1
	4.01 <sup>b</sup>	3.97	4.19	4.13	102.9
	7.71 <sup>b</sup>	7.95	8.12	8.01	103.8

<sup>a</sup> Combined reagents give no color when KI solution is tested with starch, after carrying reagents through appropriate blank procedure.  
<sup>b</sup> Value of bromine as taken includes average Br content of 100 grams of potato pulp = 0.30 mg. of Br.

cool, and extract with two 50-cc. portions of hot water, filtering the extracts into the beaker containing the previous extracts. Again add filter paper to evaporating dish, dry on hot plate, and ash in muffle at 500° C. To ash from third ignition, add sufficient dilute sulfuric acid to react with alkali and carbonate present in the ash; have little excess acid present. Filter the extract, wash twice with cold water, and rinse funnel into combined extracts. Discard filter paper and residue.

The combined extracts should be 300 to 350 cc. and show a strongly basic reaction. To test for basicity, use drop on spot plate. Do not add indicator to solution. If not sufficiently basic, add a pellet of potassium hydroxide.

Evaporate combined extracts to dryness on steam bath or low hot plate, taking care at the final stages to prevent spattering. To the dry residue from the evaporation of the water extracts add 25 cc. of stock sulfuric acid solution, dissolve residue as much as possible, and rinse into a bubbler using the stock sulfuric acid in a wash bottle as rinsing solution. Add 25 cc. of the chromic acid solution to the mixture (final volume in bubbler, 75 to 80 cc.). Add 80 cc. of 10 per cent potassium iodide solution to second bubbler, and connect in series as shown in Figure 1. Aspirate for 20 minutes at 500 to 800 cc. of air per minute. Titrate liberated iodine immediately with standard sodium thiosulfate 0.01 N, using soluble starch indicator.

TABLE II. BROMIDE CONTENT OF FRUITS AND VEGETABLES  
Following fumigation with CH<sub>3</sub>Br, in laboratory<sup>a</sup>

Sample	Before Fumiga- tion (Control)	Immedi- ately After	24 Hours After	48 Hours After	Fumigation Procedure <sup>b</sup>
<i>Mg. Br per 100 grams</i>					
White potatoes					
Peel	2.58	4.22	3.66	3.02	2 lb. of CH <sub>3</sub> Br per 1000 cu. ft. for 2 hours
Pulp	0.79	1.28	1.29	1.00	
Sweet potatoes					
Peel	1.66	3.16	3.20	3.16	
Pulp	0.55	0.99	0.98	0.90	
Green beans	0.54	7.22	4.20	4.08	
Tomatoes	Trace	1.26	1.11	0.91	
Eggplant	0.10	2.39	2.11	1.72	
Onions	Trace	0.80	0.62	0.61	
Apples (fresh)	None	0.30	0.31	0.27	
Pears (fresh)	None	0.28	Trace	None	
Dried peaches	1.44	2.31	1.86	1.60	2 lb. of CH <sub>3</sub> Br per 1000 cu. ft.
Dried apricots	0.90	1.89	..	1.18	

<sup>a</sup> Samples were in usual state. Values are not corrected for moisture content of sample. Results are average of three or more determinations on samples from same lot of material.  
<sup>b</sup> Fumigated at atmospheric pressure, temperature 20° to 25° C.

Results

In Table I are shown the result of a series of five duplicate determinations for bromide content of standard samples.

This series was carried out by procedures described in the table, in order to show the accuracy and reproducibility of results.

In Table II are shown the results of analyses for total bromide of fruits and vegetables following fumigation (at atmospheric pressure) in the laboratory with concentrations of methyl bromide approaching those used in commercial practice. These analyses show that appreciable quantities of methyl bromide are taken up by the produce during fumigation. In most cases a large part of the adsorbed gas is volatilized within 48 hours, escaping to the surrounding atmosphere.

In Table III is shown the bromide content of dried fruit following fumigation by commercial methods.

TABLE III. BROMIDE CONTENT OF DRIED FRUITS FUMIGATED UNDER COMMERCIAL FUMIGATION CONDITIONS<sup>a</sup>

Sample	Before Fumi- gation <sup>b</sup>	After Fumi- gation <sup>b</sup>	After Fumigation Followed by Hot Water Washing. Air-Dried <sup>b</sup>	Fumigation Procedure
	<i>Mg. Br per 100 grams</i>			
Seedless raisins	0.56	0.86	..	3 lb. of CH <sub>3</sub> Br per 3100 cu ft. for 15 hours
Dried unprocessed prunes	0.39	0.48	0.47	4 lb. of CH <sub>3</sub> Br per 1988° cu ft. for 15 hours
Dried processed peaches	0.40	1.97	1.20	4 lb. of CH <sub>3</sub> Br per 1988° cu ft. for 15 hours

<sup>a</sup> Samples were in usual state. Values are not corrected for moisture content of sample. Results are average of 5 determinations on samples from same lot of material.  
<sup>b</sup> Random samples taken from lot and placed in sealed cans. Shipped to laboratory for analysis.  
<sup>c</sup> Boxcar fumigation.

Discussion

The method herein outlined for the analysis of fruits and vegetables in order to determine their bromide content is applicable to most vegetable products; by a critical survey of many other methods, including various colorimetric procedures, it was found most suitable for analyzing the usual food stuffs for total bromides. Other procedures were unsuitable either because they were inaccurate at the concentrations of bromide present, or the amount of sample required was inadequate for the author's purpose.

The success of this method of analysis depends on the complete carbonization of the sample during the first ashing. A colorless filtrate should be obtained when extracting with hot water. If organic matter, charcoal, or indicators are present in the extract, low results will be obtained by reason of adsorption or combination of the bromine liberated by the chromic anhydride-sulfuric acid solution. This factor is particularly troublesome in the case of fruits of high sugar content, or dried fruits, where the material carbonizes slowly forming a compact mass. Longer heating during the initial ashing at 500° C. is the only successful method so far devised to overcome this difficulty. By raising the temperature of the initial ashing to 600° C. much quicker carbonization takes place, but there is lower average recovery of bromides from standard samples.

The separation of bromine from solutions containing chlorides and iodides described herein is based on the facts that chlorides are not affected, bromides are converted to bromine and iodides are oxidized to iodates, by the chromic anhydride-sulfuric acid mixture. The concentrations of sulfuric acid and chromic anhydride together with the temperature determine the completeness and selectivity of this method. The procedure must be carried out at room temperature (20° to 25° C.), and the acid mixtures must be cooled to this temperature.



ture before mixing with the chlorine-bromine-iodine mixture. High bromine values will be obtained if the temperature of the bromine or reagents is too high, due to the liberation of chlorine. Studies of the influence of relatively high concentrations of chlorine have been made by Baughman and Skinner (1) and others.

Losses of iodine from the potassium iodide solution are negligible if 10 per cent potassium iodide solution is used. When a second potassium iodide bubbler was connected in series with the bubbler system (Figure 1), sufficient iodine was obtained through aspiration to give only a weakly positive test with starch, when 7.41 mg. of bromine were present in the chromic acid-chromic anhydride mixture. If 1 per cent potassium iodide solution is used the iodine lost approximates 10 per cent of the total present in the sample. It has been found that the amount of chromic anhydride

adsorbed on glass and porcelain ware after washing in the usual chromic anhydride-sulfuric acid cleaning solution causes a loss of bromine through oxidation of the soluble bromides. All apparatus used in this analytical procedure should be washed with scouring powder and soap, and rinsed several times in hot water, followed by a distilled water rinse.

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## Hydrogen-Ion Activity and Buffer Capacity of Natural and Treated Waters

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THE electrometric measurement of the hydrogen-ion activity of natural and treated waters by means of the hydrogen and quinhydrone electrodes is often a difficult problem. The high resistance of the solutions, loss of carbon dioxide, polarization of the electrodes may result in serious errors, particularly in the case of waters low in dissolved solids. Furthermore, waters are often weakly buffered, which introduces possible inaccuracies in both electrometric and colorimetric methods. The glass electrode seems to be well suited for such solutions. Burton, Matheson, and Acree (4) have shown that the pH values of very dilute buffer solutions and distilled water obtained by its use check closely with values obtained by the isohydric colorimetric method. When first introduced, the cost of the necessary apparatus and the expensive technique required tended to limit its widespread use. Further developments lowering the cost and simplifying the technique have resulted in its widespread use as a new and valuable tool for the analytical chemist.

It has, however, certain limitations and errors. The relationship of e. m. f. to pH is linear over the pH range 1 to 9 when sodium-ion concentration does not exceed 0.1 molar. Above pH 9, however, the alkali cations, particularly sodium and lithium, exert errors which become very large at high pH values. Asymmetry potentials must be guarded against by frequent calibration of individual electrodes. In highly buffered solutions the solubility of the glass of the electrode is sufficient to introduce errors.

From the standpoints of both speed and ease of manipulation the quinhydrone electrode is well adapted to the determination of the pH value of natural and treated waters. However, the rapidity with which equilibrium potentials are attained and their ready reproducibility may inspire a feeling of confidence in results very seriously in error. Although the glass electrode has been investigated by many workers, results obtained by the authors have indicated certain factors in connection with its use with waters and other weakly buffered solutions which merit additional study. The order of precision is limited to that which may be obtained by the most careful worker reasonably familiar with the theoretic-

cal principles involved. The authors have investigated (1) effect of method of preparation of quinhydrone, (2) usefulness of quinhydrone reference electrodes, and (3) effect of buffer capacity of waters or diluted buffer solutions at various pH values.

### Experimental

**POTENTIOMETER ASSEMBLY.** A Leeds & Northrup student-type potentiometer was used in conjunction with a sensitive lamp and scale galvanometer. Readings were accurate to 0.1 millivolt. Standard cells were checked at frequent intervals, and the entire assembly was checked daily, using freshly prepared 0.05 molar acid potassium phthalate solution.

**QUINHYDRONE ELECTRODES.** These were prepared by fusing pieces of platinum foil 1 cm. square onto 5-cm. lengths of platinum wire which in turn were sealed in glass tubes, using a special sealing-in glass. Electrical contact was made in the usual manner by filling the glass tube with mercury. The electrodes were cleaned twice daily in hot dichromate cleaning mixture. They were then immersed for 3 minutes in boiling 10 per cent potassium bisulfite solution, after which they were thoroughly washed with distilled water and ignited to redness in the flame of an alcohol lamp before each determination. Electrodes so treated are very sensitive and yield results capable of duplication with great exactness. Since the painstaking work of Morgan, Lammert, and Campbell (8) has shown that exceedingly minute cracks may produce wide variations in potential, all determinations were made using either duplicate or triplicate electrodes which gave readings differing by not more than 0.02 pH unit.

**"ISOHYDRIC" INDICATOR SOLUTIONS.** Solutions of bromophenol blue, bromocresol green, chlorophenol red, bromocresol purple, bromothymol blue, phenol red, cresol red, and thymol blue were prepared and adjusted according to the method of Acree and Fawcett (1). Five solutions of each indicator were used, adjusted in steps of 0.3 pH unit over its useful range. They were stored in Pyrex bottles provided with Pyrex droppers.

**BUFFER COLOR STANDARDS.** All buffer color standards were prepared from Clark and Lubs buffer solutions whose pH values were carefully adjusted using the hydrogen electrode.

**COLOR COMPARATORS.** Two LaMotte Roulette comparators were used for all colorimetric determinations. With the special lighting conditions employed it was found possible to make readings to 0.05 pH unit. The technique developed by Acree and Fawcett (1) was used throughout. Because of possible loss of small amounts of carbon dioxide from some waters and as salt corrections were not applied, it is probable that the accuracy did not exceed 0.1 pH unit.



### Effect of Method of Preparing Quinhydrone

Kolthoff (5) has reported that values very much too acid are obtained when the pH of weakly buffered solutions is determined using quinhydrone prepared by Biilmann's method (3), the effect increasing with dilution and with increasing pH values. The effect is not observed with quinhydrone prepared without the use of ferric salts and Kolthoff is of the opinion that a trace of iron acts as a catalyst in promoting the formation of some acid impurity. He finds, for example, a pH value of 3.81 for 0.001 molar acid potassium phthalate solution using quinhydrone prepared by Biilmann's method, whereas that prepared without the use of ferric alum yields a value of 4.35, a difference of 0.52 pH unit. At higher values, the reported errors are much larger. With a phosphate buffer diluted to 0.008 molar and having a pH of 7.17 the reported error is  $-0.37$  pH unit, and when diluted to 0.0018 molar the reported error is  $-3.05$  pH units.

Since many natural waters are poorly buffered, such effects would be very serious. Accordingly, the work was repeated in part, using the same buffers and dilutions and essentially identical technique. Three lots of quinhydrone (A, B, and C) were prepared or secured as follows:

**Lot A.** Purchased from a leading manufacturer and prepared especially for such work. Very fine crystals and definitely superior to both B and C in rapidity of solution.

**Lot B.** Prepared by Biilmann's method (3). Two hundred grams of ferric alum were dissolved in 600 ml. of distilled water at  $65^{\circ}\text{C}$ . and the solution was filtered to remove insoluble basic salts. Fifty grams of hydroquinone were dissolved in 200 ml. of distilled water and the ferric alum solution was slowly added with constant stirring. The mixture was cooled in the icebox overnight, filtered with suction using a Büchner funnel, and washed four times with cold distilled water ( $5^{\circ}\text{C}$ .). The crystalline product was air-dried between filter papers for 24 hours and stored in a tightly stoppered brown bottle. Yield, 31 grams. The crystals were somewhat larger and less readily soluble than lot A and were difficult to wet.

**Lot C.** Prepared by the method of Valeur (10). Forty grams of quinone, prepared by oxidation of hydroquinone with sodium dichromate, were dissolved in 1000 ml. of 95 per cent alcohol. Eighty grams of hydroquinone were dissolved in 160 ml. of 95 per cent alcohol and the second solution was slowly added to the first with continuous stirring. The mixture was cooled overnight in the icebox, filtered with suction on a Büchner funnel, and the crystalline product washed twice by decantation with 100-ml. portions of ice-cold alcohol. It was then air-dried and bottled as above. Yield, 68 grams. The golden brown crystals were much larger than those of either A or B and much less readily soluble.

Arnd and Siemers (2) recommend recrystallization of quinhydrone from water at  $70^{\circ}\text{C}$ . and Schreiner (9) recrystallizes both hydroquinone and quinone from acetic acid solution and combines them in acetic acid solution.

Thirty-milliliter portions of diluted buffer solution were shaken for 2 minutes with considerable excess of solid quinhydrone in Pyrex electrode vessels fitted with rubber stoppers and placed in the thermostat at  $25^{\circ}\text{C}$ ., duplicate electrodes were introduced, and the potential was measured against a Veibel quinhydrone reference electrode. Saturated calomel electrodes were also used for many measurements.

Although a large number of measurements were made on a number of different diluted buffer solutions, the very considerable lowering of the pH values observed by Kolthoff with quinhydrone prepared with ferric alum was not encountered in a single instance. Data on Clark and Lubs phosphate buffer pH 7.00, diluted 1 to 10 and 1 to 50, were obtained, and are typical of all results obtained. For dilution 1 to 10, molarity 0.008, after shaking for 2 minutes with 200 mg. of quinhydrone, pH values 7.16, 7.16, and 7.17 were obtained for lots A, B, and C, respectively. For dilution 1 to 50 with molarity 0.0016, beginning with an excess of quinhydrone

and by repeating with washed quinhydrone, equilibrium values of 7.11, 7.12, and 7.14, respectively, were obtained. On using quinhydrone which had been stored for 18 months pH values of 7.12 and 7.05 were obtained for lots A and B, respectively. Kolthoff, using quinhydrone prepared from ferric alum, obtained for the 1 to 10 dilution of this buffer pH of 6.79 and for the 1 to 50 dilution a pH of 4.15. pH values for "satisfactory" quinhydrone were 7.16 and 7.17, respectively, practically identical with the authors'.

He also found that deviations were larger on old samples of the "unsatisfactory" quinhydrone. In order to check this point, small samples of lots A and B were stored in brown bottles for 18 months and the above determinations repeated with fresh buffer solutions. No differences were noted. It seems probable that some other impurity must have been present to yield the very low values which he consistently obtained. It is evident that great care should be taken to insure the purity of the quinhydrone used, particularly when working with weakly buffered solutions. It appears, however, that satisfactory quinhydrone may be prepared by use of ferric alum.

### Use of Quinhydrone Reference Electrodes

Veibel (11) used as a reference electrode a solution 0.1 molar in hydrochloric acid and 0.09 molar in potassium chloride, saturated with quinhydrone. He found the potential of such a half-cell to be constant to about 0.3 millivolt for 144 hours and to about 1.1 millivolt for 144 hours when measured against a standard hydrogen electrode. Such an electrode possesses several advantages over any type of calomel electrode as a reference electrode when the quinhydrone method is employed for determining hydrogen-ion activities: It can be prepared easily and quickly from materials which do not require elaborate purification; small variations in the concentration of the electrode solution have little effect upon the potential of the cell; and the cell composed of Veibel's electrode-quinhydrone electrode shows no appreciable temperature modulus. Veibel calculated that a variation of 0.5 per cent in the normality of the hydrochloric acid should change the potential by only 0.13 millivolt at  $18^{\circ}\text{C}$ ., equivalent to 0.002 pH unit. Two electrodes, E-1 and E-2, were prepared, differing by 0.3 per cent in the normality of the hydrochloric acid used. The potentials of the two cells, measured at  $25^{\circ}\text{C}$ . against a saturated calomel electrode, showed a variation of 0.001 pH unit.

TABLE I. CHANGE OF POTENTIAL OF OLD AND NEW VEIBEL QUINHYDRONE ELECTRODES WITH TIME

Age of Electrode Hours	Pyrex Glass, $\pi^a$		Soft Glass, $\pi^a$	
	E-3	E-4	E-5	E-6
3	0.0000	0.0000	0.0000	0.0000
48	-0.0006	-0.0007		
10 days	-0.0049	-0.0050	-0.0047	-0.0047
18 days	-0.0118	-0.0117	-0.0128	-0.0127

<sup>a</sup>  $\pi$  is the potential difference in volts between the old electrode and freshly prepared electrode.

Four electrodes were prepared, two of Pyrex glass, E-3 and E-4, and two of soft glass, E-5 and E-6. They were placed in the thermostat at  $25^{\circ}\text{C}$ . and their potentials compared at intervals with those of freshly prepared electrodes. The data are shown in Table I. The potentials of the old electrodes became increasingly negative to fresh electrodes, change at the end of the 18-day period being equivalent to about 0.2 pH unit. The kind of glass used for the electrode vessel had little effect upon the potential.

"ISOHYDRIC" REFERENCE ELECTRODES. Biilmann (8) indicated the possibility of employing standard buffer mixtures



as electrode solutions and thereby preparing reference electrodes of any desired potential. Such electrodes possess one decided advantage over the Veibel electrode. The equation used for calculating the pH of an unknown solution when measured against a Veibel or other quinhydrone reference electrode is:

$$pH_u = pH_r \pm \frac{\pi}{0.00019832 T_A}$$

where  $pH_u$  = pH of unknown solution  
 $pH_r$  = pH of buffer solution used in reference electrode  
 $\pi$  = potential difference between two electrodes  
 $T_A$  = absolute temperature

$\pi$  is positive when the pH of the buffer solution in the reference electrode is less than that of the unknown solution, and negative when it is greater. Any error due to temperature is a function not only of  $T_A$  but also of  $\pi$ . If  $\pi$  is small, which could be the case when the reference electrode solution has very nearly the same hydrogen-ion activity as the unknown solution, a variation in  $T_A$  may be considerable without materially affecting the result. When  $\pi$  is 34 millivolts  $T_A$  may vary 5° C. and an accuracy of 0.01 pH unit may still be obtained.

TABLE II. CHANGE OF POTENTIAL OF ACID POTASSIUM PHTHALATE QUINHYDRONE ELECTRODES WITH TIME  
(Temperature 25° C.)

Age of Electrodes Hours	$\pi^a$	
	E-7	E-8
1	-0.0006	-0.0006
2	-0.0014	-0.0014
24	-0.0042	-0.0042
60	-0.0057	-0.0057
7 days	-0.0144	-0.0142

<sup>a</sup>  $\pi$  is the potential difference in volts between the old electrode and a freshly prepared electrode of the same kind.

The rate of change of potential of such reference electrodes increases with increasing pH values of the buffer mixture used. Duplicate electrodes E-7 and E-8 were prepared using 0.05 molar acid potassium phthalate (pH = 3.97), kept in the thermostat at 25° C. and measured over a period of 7 days. The data are given in Table II.

Effect of Buffer Capacity of Waters on Determination of pH Values

When determining the pH value of weakly buffered solutions by the colorimetric method, serious errors will result unless the pH of the indicator solution is approximately the same as that of the solution tested. Obviously this effect, purposely increased by the use of indicator solutions whose pH values differ considerably from that of the solution tested, may be used to compare the buffer capacity of waters and diluted buffer solutions without titration.

The authors employed for the purpose a "wide-range" indicator composed of bromothymol blue 0.02 per cent, thymol blue 0.02 per cent, methyl red 0.01 per cent, and phenolphthalein 0.01 per cent, the solvent being 30 per cent alcohol. Three portions were adjusted to pH values 4.3, 7.2, and 10.3, respectively, by the "varying drop" method. Methyl red precipitated in the acid solution and another employing 80 per cent alcohol proved suitable. Buffer color standards in increments of 0.4 pH unit over the pH range 5.0-10.0 were freshly prepared each week, since they were not stable for a longer period. Readings were made to the nearest 0.1 pH unit. In order to compare the buffering action of natural waters with that of standard buffer solutions of approximately the same ionic strength, three Clark and Lubs buffers were used and dilutions of 1 to 10, 1 to 50, and 1 to 100 made with distilled water in equilibrium with the carbon dioxide in the air. Phthalate buffer, pH 5.80, was on the alkaline end of its range, well buffered

on the acid side but poorly buffered on the alkaline side. Phosphate buffer 7.00 was in the middle of its range and well buffered on both sides. Borate buffer 7.80 was on the extreme acid end, well buffered on the alkaline side and poorly buffered on the acid side.

It was found that when alkalinities were expressed as moles of calcium carbonate per liter, the buffering action of all waters examined equaled or exceeded that of the corresponding buffer of like molar concentration (Table III and fifth column of Table IV).

TABLE III. BUFFERING POWER OF DILUTED-BUFFER SOLUTIONS  
(Determined by means of a wide-range indicator)

Clark and Lubs Buffer, pH	Molar Conc.	Dilution Factor	Molar Conc., Diluted Buffer	pH of Indicator			$\Delta$ pH
				4.3	7.2	10.3	
5.80	0.09	1-10	0.009	6.0	6.0	6.2	0.2
7.00	0.08	1-10	0.008	7.0	7.0	7.1	0.1
7.80	0.05	1-10	0.005	7.4	7.5	7.6	0.2
5.80	0.09	1-50	0.0018	5.9	6.1	7.0	1.1
7.00	0.08	1-50	0.0016	6.9	7.1	7.3	0.4
7.80	0.05	1-50	0.0010	5.5	7.0	8.2	2.7
5.80	0.09	1-100	0.0009	5.8	6.2	8.7	2.9
7.00	0.08	1-100	0.0008	6.8	7.1	7.4	0.6
7.80	0.05	1-100	0.0005	5.0	6.9	8.4	3.4

About one thousand individual determinations were made of the pH values and buffer capacities of 105 natural and treated waters, selected to include as many different types as possible. pH values were determined both colorimetrically, using isohydric indicators, and with the quinhydrone electrode.

CORRECTION FOR "SALT EFFECT." Electrometric methods yield a value for the hydrogen-ion activity of a solution, correctly designated as  $paH$ , but still commonly called its "hydrogen-ion concentration" and designated as pH. Colorimetric methods yield a comparable value, or  $paH$ , only when the ionic strength of the unknown solution is the same as that of the buffer color standard used for matching. When the ionic strength of the solution being tested is less than that of the buffer color standards, a "salt correction" must be added to the observed colorimetric value to obtain the electrometric value, or true hydrogen-ion activity of the solution. If the reverse is true, the correction is subtracted. The authors have applied a salt correction to all colorimetric pH values, using for the purpose the best data available in the literature for each individual indicator. In applying these corrections, approximate molar concentrations were used instead of ionic strengths. The error so introduced will hardly exceed 0.05 pH unit.

The following experiment is presented as illustrative of the facts brought out by the long series of determinations. Three waters were selected, their alkalinities, expressed as calcium carbonate, being 62, 159, and 284 p. p. m. Pure carbon dioxide gas was used to adjust portions of each water to several different pH values, the free carbon dioxide being carefully determined for each portion. This gave many stages in the carbon dioxide-carbonic acid-bicarbonate equilibrium. Other portions were aerated in steps until the highest pH values to be obtained by such procedure were reached. This gave different stages in the bicarbonate-carbonate equilibrium. pH values and buffer capacities were determined as described above. The data are given in Table IV.

Results of all determinations may be summarized as follows:

1. No significant differences were noted in results obtained with lots A, B, and C of quinhydrone, as described above.
2. pH values obtained with the quinhydrone electrode were consistently lower than corrected colorimetric values.
3. For an accuracy of 0.1 pH unit, the quinhydrone electrode may be used with waters of fairly high alkalinity (approximately 300 p. p. m.) up to pH 7.5. For like accuracy, it is not suitable for waters of low alkalinity (below 100 p. p. m.) much above pH 7.0.



TABLE IV. HYDROGEN-ION ACTIVITY AND BUFFER CAPACITY OF WATERS

	Free CO <sub>2</sub> <i>P. p. m.</i>	Approx. Molar Concn.	Wide-Range Indicator		Isohydric Indicator		<i>Min.</i>	Quinhydrone Electrode		
			Ind. pH	H <sub>2</sub> O pH	Ind. pH	H <sub>2</sub> O pH		Lot A	Lot B	Lot C
Water 1, alkalinity 284 p. p. m.	174	0.004	4.3	6.3	C.P.R.		2	6.35	..	..
			7.2	6.3	(6.4)	6.45	12	6.36	..	..
	140	0.004	10.3	6.3			2	6.50	6.50	..
			4.3	6.4	B.T.B.		10	6.51	6.51	..
	75	0.004	7.2	6.4	(6.5)	6.60	2	6.74	6.75	6.75
			10.3	6.4	B.T.B.		6	6.75	6.75	6.75
	38	0.004	4.3	6.7	(6.7)	6.85	2	7.04	7.02	..
			7.2	6.7	B.T.B.		6	7.04	7.02	..
	5	0.004	10.3	6.9	(7.1)	7.10	2	7.38	7.37	7.41
			4.3	6.9	B.T.B.		6	7.37	7.37	7.40
	0	0.004	7.2	7.4	(7.4)	7.50	2	7.61	7.61	..
			10.3	7.5			6	7.59	7.59	..
	0	0.004	4.3	7.8	C.R.	7.90	2	7.78	7.80	7.80
			7.2	7.9	(7.8)		10	7.74	7.76	7.76
	0	0.004	10.3	8.0	P.R.		2	7.85	7.87	7.84
			4.3	8.0	(8.2)	8.25	6	7.82	7.84	7.82
	0	0.004	7.2	8.1	T.B.		2	6.07	..	..
			10.3	8.2	(8.2)	8.40	12	6.09	..	..
Water 2, alkalinity 159 p. p. m.	190	0.002	4.3	6.0	C.P.R.		2	6.24	..	..
			7.2	6.0	(6.0)	6.10	9	6.26	..	..
	137	0.002	10.3	6.1	C.P.R.		2	7.09	..	..
			4.3	6.1	(6.0)	6.35	9	7.09	..	..
	16	0.002	7.2	6.1	B.T.B.		2	7.56	..	..
			10.3	6.8	(7.0)	7.15	9	7.53	..	..
	0	0.002	4.3	7.0	C.R.		2	7.73	..	..
			7.2	7.8	(8.3)	8.00	9	5.92	5.86	..
	0	0.002	10.3	8.1	C.R.		2	6.52	6.52	..
			4.3	8.0	(8.3)	8.40	9	6.54	6.54	..
	126	0.001	7.2	8.2	C.P.R.		2	7.18	..	..
			10.3	8.4	(5.7)	6.00	10	7.17	..	..
Water 3, alkalinity 62 p. p. m.	28	0.001	4.3	5.7	B.T.B.		2	7.39	7.39	..
			7.2	5.9	(6.5)	6.65	9	7.37	7.38	..
	2	0.001	10.3	6.0	B.T.B.		2			
			4.3	6.4	(7.1)	7.50	10			
	0	0.001	7.2	6.5	C.R.		2			
			10.3	6.6	(8.0)	8.10	6			
	0	0.001	4.3	7.2						
			7.2	7.3						

TABLE V. EFFECT OF pH AND BUFFER CAPACITY OF WATERS ON ERROR OF QUINHYDRONE ELECTRODE

Alkalinity of Water	pH with Wide-Range Indicator	pH of Water	pH Error of Quinhydrone Electrode
284	0.0	7.0	-0.05
159	0.2	7.0	-0.05
62	0.2	7.0	-0.05
284	0.2	7.5	-0.10
159	0.2	7.5	-0.20
62	0.4	7.5	-0.30
284	0.2	8.0	-0.30
159	0.3	8.0	-0.45
62	1.1	8.0	-0.70
284	0.2	8.4	-0.55
159	0.4	8.4	-0.65
62	...	...	....

The approximate errors to be expected with the quinhydrone electrode at various pH values and with waters of alkalinities and buffer capacities as indicated are given in Table V. The second column lists the difference between the pH values obtained with wide-range indicator solutions of pH values 4.3 and 10.3. This difference is a convenient measure of the buffer capacity of the water at the particular pH value.

Three factors should be considered in seeking an explanation of these differences: (1) the ionization of hydroquinone as an acid, (2) the oxidation of hydroquinone by atmospheric oxygen in alkaline solution, and (3) the possible specific action of normal carbonates on the quinhydrone electrode.

A simple calculation shows that the pH of a 0.01 molar solution of quinhydrone in distilled water is 5.90 and that of

a 0.001 molar solution 6.40. Quinhydrone therefore exerts no effect below these values. LaMer and Parsons (6) have shown that in well buffered solutions the pH lowering due to dissociation of hydroquinone as an acid is only 0.01 pH unit at pH 8.50.

LaMer and Rideal (7) reported that in well buffered solutions reliable results may be obtained up to pH 8.00, even though hydroquinone is oxidized by atmospheric oxygen.

In view of these results, it seems improbable that the considerable errors found below pH 8.0 in the case of the waters examined were due entirely to the first two factors and the specific action of normal carbonates may have been a factor.

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ABSTRACTED from a dissertation submitted by A. P. Black in partial fulfillment of the requirements for the degree of doctor of philosophy to the Department of Chemistry, State University of Iowa.



# Measuring Oxidation of Lubricants

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INCREASE in viscosity has long been used as a measure of oil oxidation. The common procedure is to measure the viscosity of the sample in a viscometer before and after oxidation, which is usually accelerated by an elevated temperature. Simplification of apparatus and saving of time are possible by determining viscosity change in the dish used for heating the sample. This can readily be done by measuring the time for the lubricant to flow from side to side of the dish under carefully controlled conditions. This procedure permits the use of small samples, with a large ratio of surface to volume, so that the oxidation is greatly accelerated and the time of test correspondingly shortened. As an example, using 5-gram samples, the writer obtains in 2.5 hours results which normally require 100 hours with the usual (200-gram) sample.

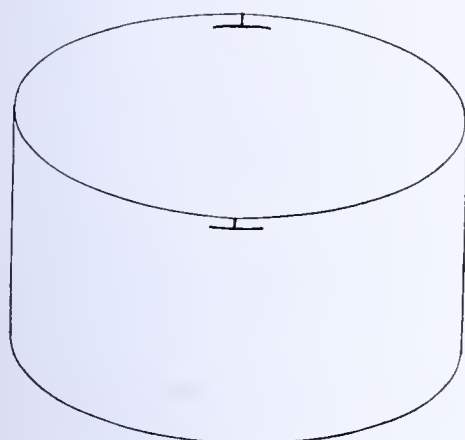


FIGURE 1

The writer has also been using this test for some time to measure the thickening of hypoid lubricants. The effect of heat on these lubricants may be more than just an oxidation, since even in the absence of oxygen certain extreme-pressure compounds may react to form a sludge (such as lead sulfide) which will thicken the lubricant. According to the writer's best knowledge the tendency of a hypoid lubricant to thicken during use is not measured directly, at the present time, but arrived at indirectly by separate determinations of sludge formation and oil oxidation. The method proposed below shows thickening tendency simply and directly.

## Apparatus

The apparatus consisted simply of an oven, a constant-temperature paraffin bath, and several glass crystallizing dishes, 80 mm. in diameter and 40 mm. deep. A straight ink line, several centimeters long, was drawn with carbon ink on the outside of each dish about 0.5 cm. from the top and parallel with the edge. A perpendicular line was drawn from this to the top of the dish, making an inverted T (Figure 1). This was repeated on the other side of the dish at a point just opposite. The horizontal line marked the stopping place for the flowing lubricant. The vertical line was used to guide its direction.

## Measurement of Flow Time

The dishes were weighed, and exactly 5 grams of sample ( $\pm 5$  mg.) were weighed into the bottom part of each dish. Each sample was allowed to come to room temperature; then the dish was

turned on its side, on a level surface, and the sample allowed to flow (the first time) past the horizontal mark to the edge of the dish. The line perpendicular to the dish edge marked the lowest point of the dish—i. e., an extension of this line would bisect the advancing wave of lubricant. The dish was set upright for about 2 seconds, then turned on the other side, until the sample flowed to the edge of the dish. These preliminary operations were for the purpose of wetting the dish with the lubricant.

Now a wrist watch (a pocket watch or stop watch would do) was held to the ear with the left wrist, and the dish was set upright for just 2 seconds (8 watch ticks, including the 0.5 second required for turning), then turned on the side first wetted. The instant the wave of sample reached the ink line parallel to the edge of the dish the dish was set upright for just 2 seconds; then it was set on the other side, and the watch ticks were counted until the wave of liquid just reached the junction of the other two lines. The dish was then set upright for 2 seconds, back to the first side, etc., in a rhythmical manner. The elapsed time was measured by counting watch ticks, while the liquid traveled from the mark on one side of the container to the mark on the other. The dish was held by the tips of the fingers, near the edge, to minimize the thermal effect from the hand. With an oil of viscosity about 90 seconds at  $210^{\circ}$  F., the following consecutive readings were obtained, at  $75^{\circ}$  F.

Number of Turn	Flow Time, Quarter Seconds
1	..
2	..
3	43
4	42
5	43
6	42

The difference in readings was due to a slight variation from a level position, either in the dish or the desk top. The recorded flow time for this sample would be 42.5 quarter seconds, with an accuracy of at least  $\pm 1$  quarter second. The readings for the first two flow times were not included, since the liquid was allowed to flow to the edge of the dish. The glass was wet with the lubricant right to the edge to permit the smooth flow of the very thin film of liquid which occasionally was seen to precede the main wave upon which measurements were being taken. If this thin film was checked by a dry glass surface beyond the ink mark the main wave was in turn slowed up, leading to erratic results.

The reproducibility of this measurement depended upon the smoothness with which the dish was turned with the right hand. With a little practice the writer was able to do this in a rhythmical manner, allowing just two watch ticks (0.5 second). The turn should be done in such a manner that the sample runs down an axis marked by the two lines perpendicular to the dish edge; any motion of the flowing liquid sideways will increase the flow time.

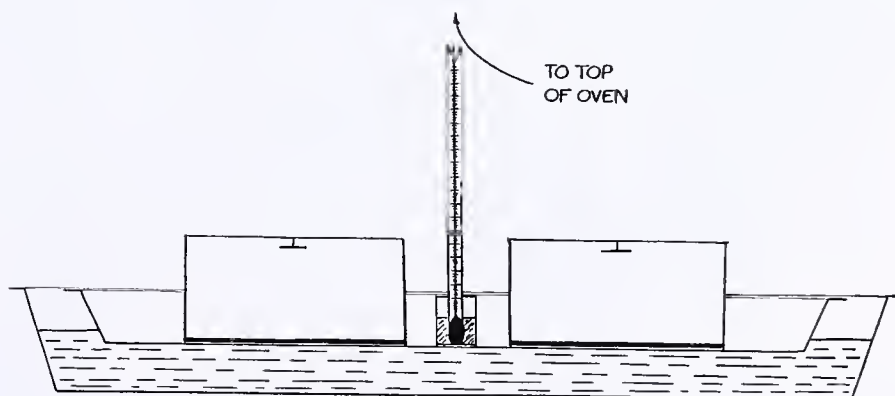


FIGURE 2. BATH FOR HEATING SAMPLES



### Heating the Samples

The temperature in the writer's oven varied markedly from point to point. At 300° F. variations in a horizontal plane 30 cm. (1 foot) above the heating coils were as much as 50° F. The use of a bath was therefore indicated.

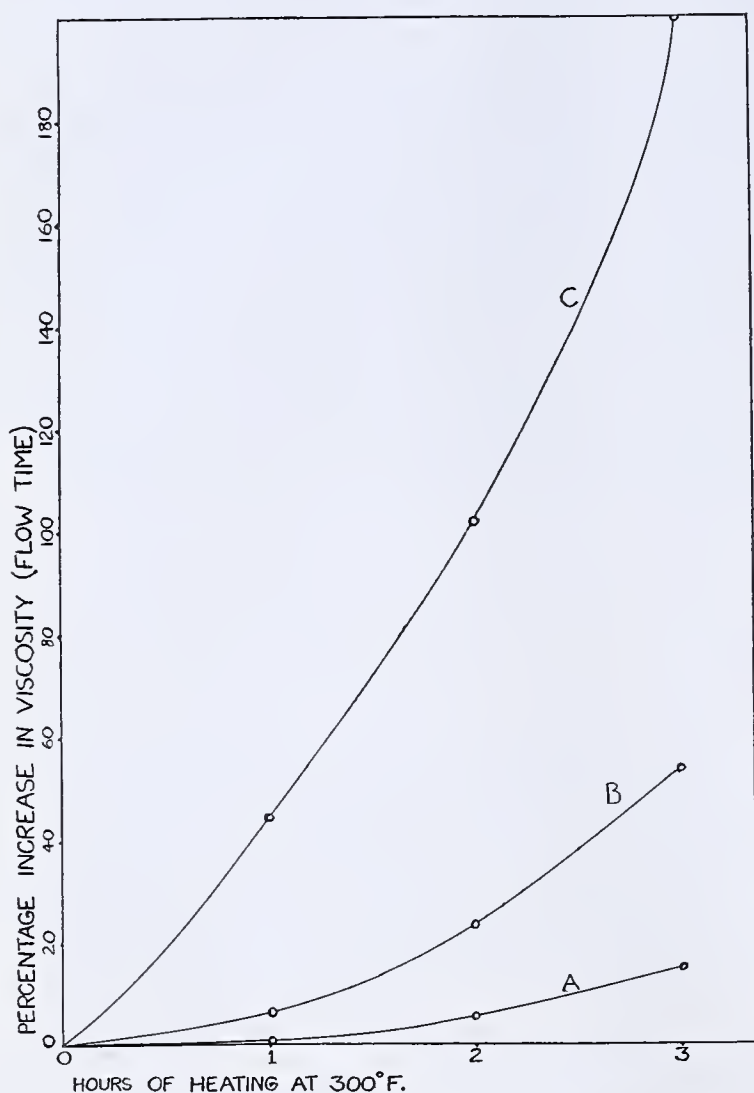


FIGURE 3. INCREASE OF FLOW TIME WITH HEATING

A 22.5-cm. (9-inch) aluminum cake pan was filled with paraffin to a depth of 2.5 cm. (1 inch), and a 20-cm. (8-inch) aluminum pie pan floated on this. The samples being heated were placed in a symmetrical position on this upper pan, assuring a level surface with the maximum interface between sample and air. If the sample dishes were floated directly on the bath they invariably tilted somewhat, giving a sample-air interface of varying area. A weighing bottle, containing oil, was placed on the center of the upper pan, and a thermometer bulb was immersed in this oil to indicate the temperature of the samples (Figure 2). The samples were preheated to approximately oven temperature before they were put into the oven. Most samples were heated for 2.5 hours at 300° F. since results obtained under these conditions seemed to be similar to those obtained in the usual 100-hour test, employing 200-gram samples. The 2.5-hour test seemed to give results higher than the 100-hour test, however, on those lubricants which oxidized excessively or formed a large amount of sludge.

### Measurement of Flow Time after Heating

The dishes were taken from the oven and allowed to stand until they came to room temperature, and the flow time was measured as before. The percentage increase in flow time,

calculated from the initial and final readings, indicated the behavior of the liquid towards oxidation, or in the case of certain hypoid lubricants, towards heat and oxidation.

### Duplication of Results

To test the reproducibility of the method, six samples of hypoid lubricant, having a viscosity of about 90 seconds at 210° F. were heated in two batches of three samples each. The initial and final flow times at 75° F. and the percentage increases in viscosity were as follows:

Sample	Initial Flow Time	Final Flow Time	Viscosity Increase %
1	40	60	50
2	39	59.5	53
3	42	63.5	51
4	41	63	54
5	39.5	61.5	56
6	40	60.5	51

These indicate that the method gives sufficiently reproducible results for many purposes.

### Discussion

The use of flow times in the manner described has at least four advantages: The change in flow time of the entire sample is determined, showing in a simple manner the tendency of the lubricant to thicken in practice. The method is time-saving. The apparatus is exceedingly simple. The sample may be reheated as many times as desired, giving a curve (flow time or percentage increase in flow time *vs.* time of heating) instead of a single result. In Figure 3 are given three examples of such curves, obtained by heating samples for an hour, measuring flow time, reheating for an hour, measuring flow time, etc. A and B were oils of viscosity 75 seconds and 75 seconds at 210° F., C was a hypoid lubricant having a viscosity of 90 seconds at 210° F. These curves do not correspond to any test commonly used at present, to the writer's best knowledge.

The directions given above assume a constant room temperature during the measurement of initial and final flow time. The writer was fortunate in having a constant-temperature room in which to measure these flow times. However, it is probable that most laboratories have available a spot which has a constant temperature for 3 or 4 hours, sufficiently constant so that a small temperature correction can be applied to the results.

If the temperature does not remain constant, two samples can be weighed out and only one heated. The initial and final flow times can then be determined at essentially the same time and temperature.

In place of the glass crystallizing dishes, various metals could be used. These should prove valuable in showing the effect of various metals and alloys upon the rate of oxidation of lubricants, as measured by the increase in flow time.

The writer makes no claim that the above method is the last word in this type of measurement, but wishes rather to call attention to the advantages of such a procedure. The method can be improved by mechanizing the manual operation of tipping the dish back and forth, and the writer hopes that some one with mechanical ability will be interested in working on such an improvement.

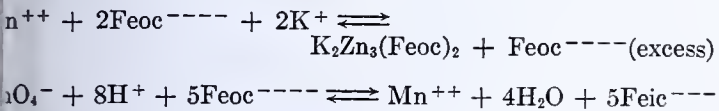
The method can be used with oils having a wide range of viscosities by varying the weight of sample—for example, the writer obtained satisfactory oxidation results on a series of light household lubricating oils using a 2-gram sample.



# Rapid Potentiometric Determination of Zinc

D. G. STURGES, Fisher Scientific Co., Pittsburgh, Penna.

THE increasing availability of apparatus for precise and convenient potentiometric titration suggests the possibility of its use in the determination of zinc. This is a common industrial analytical procedure, yet one of the most difficult. An investigation of the potentiometric titration of zinc was undertaken in the hope of finding a method at least as accurate as present ones, but more convenient and rapid. Kolthoff and Furman (2) and Kolthoff and Verzijl (3) have discussed the potentiometric titration of zinc and suggest the use of potassium ferrocyanide and potassium permanganate according to the following equations:



Tanaev (4) also investigated this method with apparent success. The initial work was a check on his procedure.

## Equipment and Procedure

The equipment used was a Fisher titrimer, a standard vacuum tube-voltmeter setup for potentiometric titration. The platinum-tungsten electrode pair was used throughout, except where otherwise noted.

TABLE I. PERMANGANATE-FERROCYANIDE METHOD  
(About 5- to 10-ml. excess of ferrocyanide was added and the solutions were titrated immediately)

Zinc Solution ML.	K <sub>4</sub> Fe(CN) <sub>6</sub> ML.	Zn Equivalent to 1 ML. of K <sub>4</sub> Fe(CN) <sub>6</sub> Gram
12	13.67	0.002634
12	13.65	0.002637
12	13.67	0.002634
24	27.35	0.002634
24	27.38	0.002631

0.025 M solution, 3 grams per liter.  
K<sub>4</sub>Fe(CN)<sub>6</sub>, approximately 0.025 M.  
KMnO<sub>4</sub>, 1 ml. ≈ 1.436 ml. of K<sub>4</sub>Fe(CN)<sub>6</sub>.

A thorough check of the permanganate-ferrocyanide method, wherein an excess of potassium ferrocyanide is added to the hot zinc solution and the excess is then titrated potentiometrically with potassium permanganate, showed certain undesirable features.

In low concentrations excellent results were obtained, as shown in Table I. As the zinc concentration was increased, however, it became more difficult to obtain consistent results. In many instances no distinct end point was observable. An investigation was then conducted to determine the source of these difficulties.

It was found, as is pointed out by Kolthoff (1), that the presence of hydrochloric acid tended to decrease the inflection potential, sufficiently in many instances to obscure the end point. To obviate this, samples dissolved in hydrochloric and perchloric acids were neutralized with ammonium hydroxide and acidified to approximately 1.5 N with sulfuric acid.

In those determinations run above 70° C. a perceptible odor of hydrocyanic acid indicated the necessity of maintaining the temperature below this point. Acid concentration as high as 2 N produced no appreciable differences. The effect of higher acidity was not studied.

In an effort to avoid any possible effects due to breakdown of the permanganate, ceric sulfate was substituted as the oxidizing agent. A study of the ceric sulfate-ferrocyanide titration showed a large inflection potential (Figure 1) which was somewhat sharper than that obtained with permanganate.

Excellent reproducibility was obtained in standardization of the ferrocyanide solution, and the results obtained with three samples of pure zinc are shown in Table II. The zinc used was C. P., granular, 40-mesh.

TABLE II. RESULTS WITH PURE ZINC

Sample Gram	K <sub>4</sub> Fe(CN) <sub>6</sub> ML.	Zn Equivalent to 1 ML. of K <sub>4</sub> Fe(CN) <sub>6</sub> Gram
0.1094	38.92	0.002811
0.1065	37.90	0.002810
0.1038	38.61	0.002806

Erratic results were obtained with a series of commercial zinc samples and a search for the causes was undertaken. Here as in the permanganate back-titration, hydrochloric acid seemed to decrease the inflection potential, but did not affect the precision.

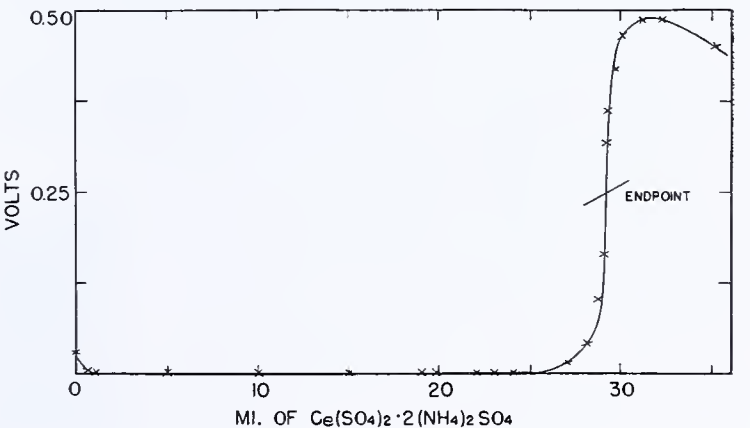


FIGURE 1. TITRATION OF APPROXIMATELY 0.025 M POTASSIUM FERROCYANIDE WITH APPROXIMATELY 0.02 N CERIC AMMONIUM SULFATE

If the ferrocyanide was added to a hot solution of zinc and the excess titrated immediately, there was no effect on the precision as long as operation was normal. However, at times the electrodes behaved erratically and the observable formation of hydrocyanic acid made it obvious that such a procedure is not to be encouraged.

TABLE III. EFFECT OF PHYSICAL HANDLING OF SOLUTIONS

Sample Gram	K <sub>4</sub> Fe(CN) <sub>6</sub> ML.	Zn Equivalent to 1 ML. of K <sub>4</sub> Fe(CN) <sub>6</sub> Gram
No. 1. Cold, back-titrated immediately		
0.1013	43.70	0.002316
0.1056	44.55	0.002370
0.1048	44.50	0.002355
0.1031	44.33	0.002326
		Av. 0.002342
No. 2. Cold, stood 15 minutes after addition of excess Feoc <sup>----</sup> ; then back-titrated		
0.1052	44.71	0.002353
0.1013	42.94	0.002359
0.1029	43.74	0.002353
0.1031	43.88	0.002350
0.1035	43.97	0.002354
		Av. 0.002353
No. 3. Hot, back-titrated immediately		
0.1051	44.31	0.002372
0.1022	43.84	0.002331
0.1036	44.27	0.002340
		Av. 0.002348
No. 4. Same as No. 2 but run hot		
0.1002	43.28	0.002315
0.1056	44.45	0.002376
		Av. 0.002345



TABLE IV. ANALYSIS OF COMMERCIAL ZINC SAMPLES

	Sample Gram	K <sub>2</sub> Fe(CN) <sub>6</sub> Ml.	Zinc %
Zinc mossy	0.1024	40.10	97.15
	0.1046	40.90	97.01
	0.1028	40.13	96.95
	0.1030	40.27	97.00
	0.1041	40.67	96.93
			Av. 97.01
Zinc dust, No. 1	0.1011	39.25	96.32
	0.1026	39.82	96.32
			Av. 96.32
Zinc dust, No. 2	0.1040	40.55	96.74
	0.1033	40.30	96.79
			Av. 96.77
Zinc die casting	0.1044	40.15	95.43
	0.1010	38.95	95.67
	0.1040	40.10	95.66
			Av. 95.59

Ammonium chloride had no effect. Sulfuric acid up to 2 *N* caused no appreciable differences.

It seemed possible that the dense potassium zinc ferrocyanide precipitate was affecting the tungsten electrode. However, no satisfactory results could be obtained with a polarized platinum-platinum electrode pair.

Finally it was decided to vary the physical handling of the solutions, in an effort to determine whether these factors were responsible for the difficulties.

Four procedures were investigated. In each instance the samples were dissolved in hydrochloric acid and diluted to 150 ml. with distilled water. The excess hydrochloric acid was neutralized with ammonium hydroxide and the solution made acid with 1 to 1 sulfuric acid. At this point two of the procedures involved adding an excess of potassium ferrocyanide to the cold solution, in the first, titrating the excess ferrocyanide immediately with approximately 0.02 *N* ceric ammonium sulfate; in the second, titrating the excess after the solution had been allowed to stand 15 minutes. A similar procedure was followed with two series of solutions which were heated to 70° C. The results obtained are shown in Table III.

A further check confirmed the results shown in the second part of Table III—that is, that by permitting the cold solutions to stand for 15 minutes after the excess ferrocyanide has been added, a high order of precision is obtainable. This would seem to be in line with the known low velocity of attainment of electrochemical equilibrium of ferrocyanide-zinc solutions (2).

The method as outlined was applied to the analysis of commercial zinc samples. The solutions were allowed to stand 15 minutes before titration, as indicated in Table III. The results are given in Table IV.

Potassium permanganate was then substituted for ceric sulfate in the procedure. The results obtained were much less satisfactory.

### Summary

The volumetric determination of zinc, by adding an excess of potassium ferrocyanide and back-titrating the excess potentiometrically with ceric sulfate, using a platinum-tungsten electrode pair, can be carried out with a precision equivalent in magnitude to methods employing external or internal indicators.

The actual titration can be done with much greater speed than can be attained using indicators. The 15-minute period required to allow the solutions to come to equilibrium after the addition of excess ferrocyanide, is of no disadvantage where a large number of samples are to be treated, since the first ones treated with ferrocyanide will be ready for titration when the excess reagent has been added to all the samples.

Potassium permanganate is a satisfactory oxidizing agent for ferrocyanide where the zinc concentration is not in excess of 20 to 30 mg. per 100 ml. Above this concentration the system behaves erratically.

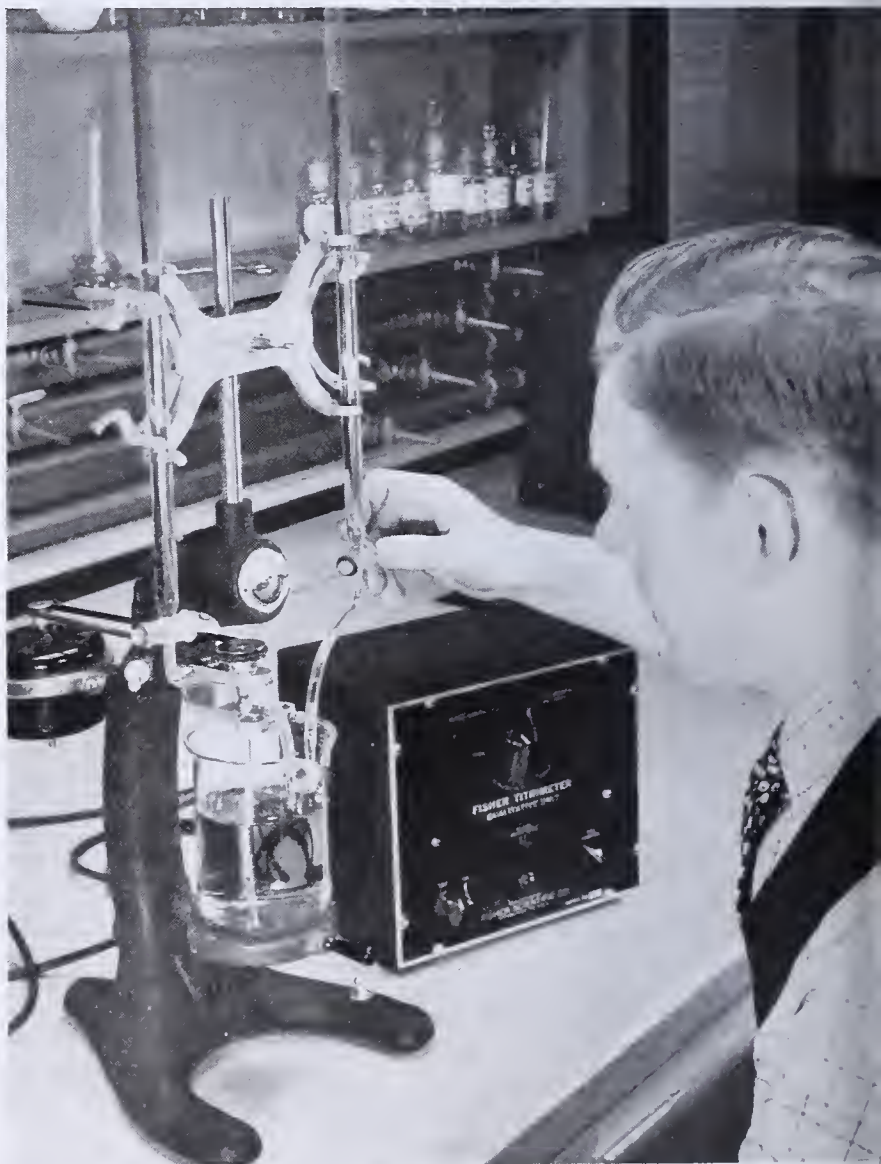
Hydrochloric acid decreases the inflection potential sufficiently, with both ceric sulfate and potassium permanganate to make the end point difficult to obtain.

The titration should be carried out at room temperature and the solutions allowed to stand 15 minutes before titrating the excess ferrocyanide.

Addition of the potassium ferrocyanide to a hot zinc solution should be avoided because of decomposition of the ferrocyanide at even moderately high temperatures.

### Literature Cited

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- (2) *Ibid.*, p. 324.
- (3) Kolthoff, I. M., and Verzijl, E. J. A. H., *Rec. trav. chim.*, 380 (1924).
- (4) Tanaev, I., *J. Applied Chem. (U. S. S. R.)*, 5, 86 (1932).



APPARATUS FOR ELECTROMETRIC DETERMINATION OF ZINC



# Tetraphenylarsonium Chloride as an Analytical Reagent

## Determination of Mercury, Tin, Cadmium, and Zinc

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Mercuric ion (0.5 to 100 mg.) can be quantitatively precipitated as  $[(C_6H_5)_4As]_2HgCl_4$  by tetraphenylarsonium ion in a 1.0 to 2.5 *M* sodium chloride solution in a volume of 30 to 120 ml. The determination cannot be made gravimetrically, but only by titrating potentiometrically the excess of reagent with iodine. Free acid, 0.2 to 1.0 *M*, except nitric acid, does not interfere. The precipitate does not form in alkaline solution.  $MnO_4^-$ ,  $ReO_4^-$ ,  $ClO_4^-$ ,  $IO_4^-$ ,  $I^-$ ,  $Br^-$ ,  $F^-$ ,  $WO_4^{--}$ ,  $MoO_4^{--}$ ,  $CrO_4^{--}$ ,  $CNS^-$ ,  $Bi^{+++}$ ,  $Pt^{++++}$ ,  $Sn^{++++}$ ,  $Zn^{++}$ ,  $Cd^{++}$ ,  $Tl^{+++}$ , and those ions that react with iodide ion or with iodine interfere. Interference by  $Cu^{++}$ ,  $Sn^{++++}$ ,  $Mn^{++}$ ,  $Fe^{+++}$ , and  $Ti^{++++}$  may be eliminated by the formation of certain stable complex ions.

Tin (0.80 to 84.0 mg.) in a volume of 30 to 120 ml. can be determined quantitatively by precipitation as  $[(C_6H_5)_4As]_2SnCl_6$  with an excess of standard tetraphenylarsonium chloride and the subsequent potentiometric titration of the excess with iodine, or by the direct potentiometric titration of the

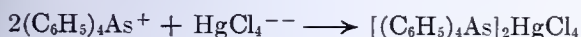
dissolved precipitate. The precipitate should be formed in a solution 0.4 to 2.0 *M* in hydrochloric acid and 1.5 to 3.0 *M* in sodium chloride, depending upon the quantity of precipitate, and allowed to stand 30 to 60 minutes before filtering.  $Fe^{+++}$ , more than 25 mg. of  $Fe^{++}$ ,  $Pt^{++++}$ ,  $Au^{+++}$ ,  $Bi^{+++}$ ,  $Hg^{++}$ ,  $Cd^{++}$ ,  $Zn^{++}$ ,  $Tl^{+++}$ ,  $Sb^{+++}$ ,  $As^{+++}$ ,  $UO_2^{++}$ ,  $F^-$ ,  $C_2O_4^{--}$ ,  $PO_4^{--}$ , acetates, citrates, alkaline substances and all anions precipitated by the reagent must be absent.

Cadmium and zinc may be quantitatively determined by precipitation with an excess of tetraphenylarsonium chloride in 3.0 to 3.5 *M* sodium chloride solution, and the subsequent potentiometric titration of the excess with iodine. The precipitates are somewhat more soluble than those of mercury and tin formed under similar conditions. In addition to those ions which interfere in the determination of tin, interference by manganese, cobalt, copper, and iron is more serious here. Interference by small amounts of tin may be avoided by the addition of tartrate.

THE potentiometric titration of tetraphenylarsonium chloride with iodine, upon which determinations of mercury, stannic, cadmium, and zinc ions depend, has been discussed in a previous paper (2).

### Determination of Mercury

In the presence of an excess of chloride ion the mercuric ion forms the complex halide ion,  $HgCl_4^{--}$ . The determination of mercury with tetraphenylarsonium ion depends upon the reaction



The compound is white and crystalline, insoluble in sodium chloride solution, but fairly soluble in water.

A gravimetric determination was not feasible, since no suitable wash liquid could be found. The tetraphenylarsonium compounds of the mercuric complexes of the other halogens behave similarly, but are not suitable for analytical work since tetraphenylarsonium bromide and iodide are precipitated also.

Although a gravimetric determination is impossible, mercury can be determined by precipitating the compound with an excess of standard reagent in sodium chloride solution and, after filtering the precipitate, titrating the excess of reagent potentiometrically with iodine, in the manner already described (2). The method is rapid and accurate. A direct potentiometric titration between the mercuric and tetraphenylarsonium ions was found to be impossible. Lamprey (3) reported a conductometric determination based on this reaction but showed no data in support.

For this work standard solutions of tetraphenylarsonium chloride, mercuric ion, and iodine were required. The 0.01 to

0.03 *N* iodine solution, standardized by means of arsenite, contained 6 to 8 grams of potassium iodide per liter. The 0.01 to 0.03 *M* tetraphenylarsonium chloride solution was made by dissolving 5 to 10 grams of reagent per liter and standardizing it potentiometrically with standard iodine (2). The mercuric solution was made by dissolving 5.1106 grams of pure mercury in 50 ml. of 50 per cent nitric acid. The solution was boiled to remove nitrous fumes, the excess nitric acid was neutralized with sodium hydroxide, and the solution was diluted to 1000 ml. after being slightly acidified with hydrochloric acid.

**PROCEDURE.** The solution of mercuric ion, prepared as described, is diluted to about 30 ml. and enough commercial (non-iodized) sodium chloride is added to form a 1.0 to 2.5 *M* solution after the addition of the tetraphenylarsonium chloride. Standard 0.01 to 0.02 *M* reagent, in not more than 10-ml. excess, is added during constant stirring. The volume should now be 60 to 120 ml., depending upon the quantity of mercury present. The precipitate is allowed to stand 15 to 60 minutes and filtered through a Gooch crucible. The precipitate is washed several times with saturated sodium chloride solution, and the filtrate and washings are titrated potentiometrically with standard iodine as already described.

This titration determines the excess of standard tetraphenylarsonium chloride used and, by difference, the volume of reagent required to remove the mercury quantitatively. The quantity of mercury present is determined by this volume of reagent and is calculated from the standardization of iodine with arsenious oxide, the volume of tetraphenylarsonium chloride equivalent to 1 ml. of standard iodine, and the equation given above. One milliliter of 0.01 *M* tetraphenylarsonium chloride is equivalent to 1.0031 mg. of mercury.

The error involved in determining quantities of mercury from 0.5 to 107 mg. in pure solutions is about  $\pm 0.06$  mg.

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For the larger quantities, 1.1 *M* and for the smaller, 2.5 *M* sodium chloride are most suitable. If the precipitate is small a considerable excess of reagent and several hours' standing are desirable. The presence of solid tetraphenylarsonium chloride is shown by the appearance of long needlelike crystals.

The most important factors studied were (1) the most suitable sodium chloride concentration, (2) the most suitable excess of reagent, (3) the proper volume for precipitation, (4) the time the precipitate should stand before being filtered, (5) the limits of the efficiency of the method, and (6) the influence of the presence of other substances.

**EFFECT OF SODIUM CHLORIDE CONCENTRATION.** The most satisfactory concentrations are between 1.0 *M* and 2.5 *M*. In these concentrations the precipitate is composed of much larger crystals and is therefore more easily transferred. Precipitation is incomplete in lower concentrations. In higher concentrations tetraphenylarsonium chloride may precipitate with the chloromercuriate compound, if a considerable excess is present.

TABLE I. EFFECT OF VARIOUS ANIONS

(Mercury present, 25.64 mg.; volume, 60 ml.; 7.85 ml. excess reagent)

NaCl, <i>M</i>	Addition Agent Salt	<i>M</i>	Mercury Found <i>Mg.</i>	Mercury Error <i>Mg.</i>
2.3	NaNO <sub>3</sub>	0.7	25.77	+0.13
2.3	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.0	25.66	+0.02
2.3	NaOAc	1.0	25.68	+0.04
2.3	NaHCO <sub>3</sub>	3.0	25.67	+0.03
1.1	Na <sub>2</sub> HPO <sub>4</sub>	0.5	25.61	-0.03
1.1	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	0.1	25.64	0.00
1.1	K <sub>2</sub> C <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	0.1	25.62	-0.02
1.1	Na <sub>2</sub> C <sub>6</sub> H <sub>4</sub> O <sub>7</sub>	0.2	25.69	+0.05
1.1	NaNO <sub>3</sub>	0.1	...	...
	Na <sub>2</sub> SO <sub>4</sub>	1.0	25.80	+0.16
1.1	NaNO <sub>3</sub>	1.0	...	...
	Na <sub>2</sub> SO <sub>4</sub>	0.2	25.68	+0.04
2.3	NaNO <sub>3</sub>	0.1	...	...
	Na <sub>2</sub> SO <sub>4</sub>	0.1	...	...
	NaOAc	4.0	25.76	+0.12
	<i>Gram</i>			
1.1	H <sub>2</sub> SeO <sub>3</sub>	1.0	25.71	+0.07
1.1	K <sub>2</sub> TeO <sub>3</sub>	1.0 TeO <sub>2</sub>	25.72	+0.08

**EFFECT OF VARYING EXCESS OF TETRAPHENYLARSONIUM CHLORIDE.** Since the solubility of tetraphenylarsonium chloride decreases greatly with increased sodium chloride concentration (2), a greater excess may be used if the chloride concentration is fairly low. The permissible excess also is less with the higher concentrations of mercury. Therefore, if the quantity of mercury is large, requiring a large volume of reagent, the sodium chloride concentration should be about 1.0 *M* for best results. Since tetraphenylarsonium chloride is almost quantitatively insoluble in 3.0 *M* sodium chloride, the permissible excess of reagent under these conditions is very low, and the precipitate must be filtered almost immediately. From 2 to 15 ml. of 0.01 to 0.02 *M* tetraphenylarsonium chloride may be used in excess in salt concentrations between 1.0 and 2.5 *M*. Since it is impossible to tell when an excess of reagent has been added, a preliminary determination should be made to determine the approximate quantity of mercury.

**EFFECT OF VOLUME.** The total volume in which the precipitation is made should be kept as low as possible, so that the filtrate and washings will not exceed 100 ml., in order to secure the best conditions for titrating the excess of reagent with standard iodine. Satisfactory results were obtained, however, in volumes varying from 30 to 200 ml. Only the larger quantities of mercury were precipitated in volumes greater than 100 ml. The precipitate is somewhat more crystalline in the larger volumes. For practical purposes, depending upon the quantity of mercury, the volume was 60 to 120 ml. If there was less than 5 mg. of mercury the volume was still smaller.

If the solution is heated the precipitate is more crystalline, but filtrations must always be made at room temperatures.

**EFFECT OF TIME OF STANDING.** For a moderate excess of reagent the time seems of no considerable importance. In general, if the quantity of precipitate is large filtration should take place soon after the solutions are thoroughly mixed. If the amount of precipitate is small 15 to 60 minutes should elapse.

**EFFECT OF ACIDITY.** The precipitate is somewhat soluble in acid of high concentration. Therefore the mercury solution must be neutralized with sodium bicarbonate or sodium hydroxide, then sufficient hydrochloric acid added to make the solution 1 *M*, after which the sodium chloride and reagent are added. In 1 *M* hydrochloric acid better results are secured with 2.3 *M* sodium chloride. Higher acid concentrations retard precipitation. Nitric and sulfuric acids behave in the same way, but all free nitric acid must be removed before the filtrate is titrated with iodine. The organic acids interfere more seriously than others, but, in general, 0.2 *M* acids of any kind are not detrimental to the process. Free alkalies and ammonia prevent precipitation.

**INTERFERING SUBSTANCES.** Most of the common anions except nitrate in rather high concentration, do not interfere. Nitrate causes the precipitation of tetraphenylarsonium nitrate. Those anions which react with tetraphenylarsonium ion—MnO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>-</sup>, WO<sub>4</sub><sup>-</sup>, MoO<sub>4</sub><sup>-</sup>, IO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, ReO<sub>4</sub><sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup>, F<sup>-</sup>, and CNS<sup>-</sup>—and those that react with iodine with iodide ion must be absent.

Cations that form halide complexes, and consequently precipitate with tetraphenylarsonium ion—Bi<sup>+++</sup>, Sn<sup>+++</sup>, Pt<sup>++++</sup>, Au<sup>+++</sup>, Tl<sup>+++</sup>, Zn<sup>++</sup>, Cd<sup>++</sup>, and Fe<sup>+++</sup>—and those that oxidize iodide ion or reduce iodine must be absent. The addition of certain substances to form stable complex ions may permit the presence of certain of these interfering cations as Table II shows. High concentrations of manganese interfere. Ferrous ion interferes with the titration of the excess reagent unless the end point is known approximately and is quickly reached. The influence of certain cations is shown in Table II.

TABLE II. EFFECT OF VARIOUS METALLIC IONS

(Mercury present, 25.64 mg.; 60-ml. volume; 7.85 ml. excess reagent)

NaCl, <i>M</i>	Addition Agent Salt	<i>M</i>	Mercury Found <i>Mg.</i>	Mercury Error <i>Mg.</i>
2.3	Mg(OAc) <sub>2</sub>	1.0	25.58	-0.06
None	AlCl <sub>3</sub>	1.1	25.73	+0.09
None	BaCl <sub>2</sub>	1.1	25.67	+0.03
None	CaCl <sub>2</sub>	1.1	25.67	+0.03
1.1	CoSO <sub>4</sub>	0.25	25.67	+0.03
1.1	CrCl <sub>3</sub>	1 g.	25.60	-0.04
1.1	FeSO <sub>4</sub>	0.5	25.64	0.00
None	MnCl <sub>2</sub>	0.6	25.81	+0.17
1.1	MnCl <sub>2</sub>	0.1	25.71	+0.07
None	NH <sub>4</sub> Cl	2.3	25.60	-0.04
1.1	PbCl <sub>2</sub>	0.5	25.67	+0.03
1.1	NiSO <sub>4</sub>	0.25	25.66	+0.02
1.1	UO <sub>2</sub> (OAc) <sub>2</sub>	0.1	25.73	+0.09
1.1	ZrOCl <sub>2</sub>	0.05	25.56	-0.08

Cupric ion does not interfere with the precipitation of the mercury compound, but interferes with the titration of the filtrate by oxidizing iodide ion to iodine. This interference may be avoided, as Table III shows, by adding sodium citrate and citric acid before titrating. Tartrate is not effective with copper, but is effective, if added before precipitation, in eliminating interference by manganese and stannic ions, for which citrate is not effective. Titanium, in the form of the double oxalate, does not interfere.

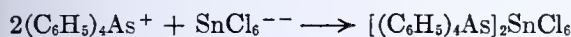
Interference by ferric ion is best avoided by adding, before precipitating the mercury compound, about 0.5 ml. of syrupy phosphoric acid per 100 mg. of ferric ion, or until the yellow color is removed. After the removal of the mercury precipitate, the quantity of acid is doubled and an equal weight of disodium phosphate added. Thereupon the titration is carried out as usual. This treatment is effective for as much



300 mg. of ferric ion. Fluoride cannot be used for this purpose because of the slight solubility of a tetraphenylarsonium compound. Interference by more than traces of lithium, zinc, and bismuth cannot be eliminated.

### Determination of Tin

In slightly acid solution, containing an excess of chloride, quadrivalent tin is precipitated completely by tetraphenylarsonium ion. The precipitated tetraphenylarsonium stannate,  $[(C_6H_5)_4As]_2SnCl_6$ , is white, crystalline, soluble in water and alkalis, but insoluble in concentrated chloride solutions. The precipitation is due to the reaction



In very weakly acid solutions is incomplete and somewhat colloidal.

As in the case of mercury, the determination cannot be made gravimetrically since no suitable wash liquid has been found. Neither can it be determined by a direct potentiometric titration between the two ions, although it is possible to determine the tin by titrating the dissolved precipitate potentiometrically with iodine. The most practical method, however, is the same as that for the determination of mercury—precipitation of the tin with an excess of standard tetraphenylarsonium chloride and potentiometric titration of the excess with standard iodine.

TABLE III. ELIMINATION OF INTERFERENCE BY CERTAIN IONS  
(Mercury present, 25.64 mg.; 60-ml. volume; NaCl 1.1 to 2.3 M)

Mercury Present Mg.	Addition Agent	Mercury Found Mg.	Mercury Error Mg.
400	Sodium citrate, 3 grams	25.67	+0.03
1900	Citric acid to acidify		
32	Potassium tartrate, 4.7 grams	25.74	+0.10
32	Potassium tartrate and tartaric acid	25.65	+0.01
90	Sodium oxalate and HCl	25.69	+0.05
21	Disodium phosphate, 2 grams	25.67	+0.03
103	$H_3PO_4$ , 2 ml.		
103	Disodium phosphate, 2 grams	25.64	0.00
206	$H_3PO_4$ , 2 ml.		
206	Disodium phosphate, 2 grams	25.69	+0.05
309	$H_3PO_4$ , 2 ml.		
309	Disodium phosphate, 3 grams	25.69	+0.05
515	$H_3PO_4$ , 2 ml.		
515	Disodium phosphate, 3 grams	Unsatisfactory	

The titration indicates by difference the volume of reagent required to precipitate the tin. From the equation it is seen that 1 ml. of 0.01 M tetraphenylarsonium chloride is equivalent to 0.5935 mg. of tin.

Three standard solutions were required in this investigation—0.02 to 0.03 N iodine, 0.01 to 0.02 M tetraphenylarsonium chloride, and a standard tin solution. The first two solutions were made in the manner already described (2). The tin solution was made by dissolving 1.9705 grams of pure tin in concentrated hydrochloric acid while a slow stream of chlorine was passed through the gently boiling solution. When the metal was dissolved completely the excess of chlorine was expelled by a current of air, and the solution was cooled and diluted to 500 ml. Thus, each milliliter contained 4.1 mg. of tin and a small amount of acid.

PROCEDURE. To the tin solution, in as small volume as possible, 2 ml. of concentrated hydrochloric acid and enough commercial noniodized sodium chloride are added to give a 2.5 to 3 M concentration of sodium chloride in a final volume of 60 ml. A measured volume of standard tetraphenylarsonium chloride, known to be in excess, and enough water to give a volume of 100 ml. are added during constant stirring. If additional tetraphenylarsonium chloride is needed to complete the precipitation additional salt need be added, but the acid concentration should always be 0.4 to 1.0 M. The concentration of sodium chloride

should be 2.5 to 3.0 M for quantities of tin up to 30 mg. and may drop to 1.5 to 2.0 M for larger quantities.

When the precipitate has settled completely and has stood 30 to 60 minutes, it is filtered through a Gooch crucible and washed several times with saturated sodium chloride. The combined filtrate and washings are titrated potentiometrically with standard iodine (2) to determine the excess of reagent. If there is a large quantity of precipitate it is not necessary that it stand so long before filtering.

The factors studied in this determination are the same as those studied in the determination of mercury.

EFFECT OF SODIUM CHLORIDE CONCENTRATION. The concentration required for quantitative precipitation of the tin compound is higher than that required in the determination of mercury. Good results were obtained with sodium chloride concentrations between 2.5 and 3.5 M. With high concentrations only a very small excess of reagent may be used and the precipitate must be filtered very quickly to avoid precipitating some of the reagent. For large quantities of tin the sodium chloride concentration need not be greater than 2.0 M.

INFLUENCE OF ACIDITY. Unless the mixture has a certain minimum acidity the precipitate is somewhat colloidal, probably because of hydrolysis. To secure good results the solution should be at least 0.4 M with hydrochloric acid, and the concentration may be as high as 2.0 M. There is no precipitation in alkaline or neutral solutions.

Since the sodium chloride concentration is higher than in the mercury determination, the maximum excess of reagent must be less. The excess should never be greater than 10 ml. of 0.015 M reagent, preferably less in 2.5 to 3.0 M sodium chloride, to avoid precipitating the reagent.

The mixture must be well stirred and the precipitate permitted to settle completely. This should require not less than 15 minutes nor more than 60 minutes for average quantities of tin. If the precipitate is bulky, as in the case of quantities of tin greater than 50 mg., this time may be shortened. For very small precipitates more time may be required. For average amounts, good results were obtained by filtering after 45 minutes.

As in the case of mercury, the least possible volumes were used for best results—from 30 to 120 ml., depending upon the quantity of tin present. Most determinations were carried out in a volume of 60 ml.

Heating the mixture offers no advantage other than to cause the precipitate to form more slowly and in larger crystals. The filtration should never be made at temperatures higher than room temperature.

Three to 8 ml. of excess reagent were used in all the determinations. A series of results not recorded here showed that 0.80 to 84.0 mg. of tin was determined with an error of  $\pm 0.06$  mg. A 3- to 8-ml. excess of reagent was used in all cases. The determination of quantities larger than 84 mg. of tin is hindered by the bulkiness of the precipitate, making it difficult to filter and wash, and increasing the probability of adsorbing some of the reagent.

INTERFERING SUBSTANCES. Substances that interfere with the determination of tin by tetraphenylarsonium ion fall generally into three classes: (1) those that prevent the complete precipitation of the tin compound, (2) those that are precipitated by the reagent, and (3) those that interfere with the iodine titration. To the first class belong all those substances which react with tin to form complexes, such as phosphate, citrate, oxalate, and fluoride, and those that render the solution alkaline or neutral, such as sodium hydroxide, sodium bicarbonate, and neutral buffers. To the second class belong such anions and cations as perrhenate, permanganate, periodate, perchlorate, iodide, bromide, fluoride, tungstate, chromate, thiocyanate, platinum, ferric, bismuth, thallic, mercuric, cadmium, zinc, and auric. In the third class are those that



reduce iodine or oxidize iodide ion, such as stannous, anti-mony, nitrate, cupric, and ferric.

It is necessary that all substances of the three classes, except cupric and nitrate ions, be absent in these determinations. Interference by cupric ion may be avoided by adding sodium citrate and citric acid, as with mercury, but the addition must not be made until the tin precipitate has been removed. All free nitric acid must be neutralized before the potentiometric titration.

TABLE IV. EFFECT OF CERTAIN ANIONS

(20.98 mg. of Sn; 2.5 M NaCl; 60-ml. volume; constant-volume reagent. Concentrated acids used in every case)

Added Substances	Tin Found Mg.	Tin Error Mg.
HCl, 2 ml.	20.98	0.00
HNO <sub>3</sub> , 2 ml.	20.99	+0.01
NaNO <sub>3</sub> , 4 grams	21.03	+0.05
HCl, 2 ml.		
H <sub>2</sub> SO <sub>4</sub> , 2 ml.	21.06	+0.08
H <sub>2</sub> SO <sub>4</sub> , 5 ml.	20.96	-0.02
Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O, 5 grams	20.95	-0.03
HCl, 2 ml.		
Acetic acid, 2 ml.	20.96	-0.02
Acetic acid, 5 ml.	20.71	-0.27
Acetic acid, 5 ml.	20.90	-0.08
HCl, 2 ml.		
Sodium acetate, 4 grams	No precipitate	
HCl, 2 ml.		
H <sub>3</sub> BO <sub>3</sub> , 0.7 gram	20.97	-0.01
Tartaric acid, 2 grams	20.49	-0.49
Tartaric acid, 2 grams	20.95	-0.03
HCl, 2 ml.		
Potassium tartrate, 2 grams	20.89	-0.09
HCl, 2 ml.		
Citric acid, 4 grams	No precipitate	
HCl, 2 ml.		
H <sub>3</sub> PO <sub>4</sub> , 2 ml.	10.61	-10.37
Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O, 4 grams	No precipitate	
HCl, 2 ml.		
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , 1 gram	Precipitation incomplete	
HCl, 2 ml.		
NH <sub>4</sub> F, 1 gram	Precipitation incomplete	
HCl, 2 ml.		

Organic acids and phosphoric acid interfere. The presence of hydrochloric acid with acetic or tartaric acid largely eliminates this interference, but has no effect with acetates, citric acid or citrates, phosphates, oxalates, or fluorides.

Table V shows the effect of certain cations. No way could be found to avoid interference by ferric ion since stannic and ferric ions form similar complexes. Ferrous ion apparently does not interfere with the precipitation of the tin compound, but satisfactory end points could not be obtained in the titrations when more than 25 to 35 mg. of ferrous ion were present. Uranyl ion interferes.

TABLE V. EFFECT OF CERTAIN CATIONS

(20.98 mg. of Sn; 2.5 M NaCl; 0.4 N HCl; 25 ml. of 0.015 M reagent; volume, 60 ml.)

Added Substance	Tin Found Mg.	Tin Error Mg.
Al <sup>+++</sup> , 0.3 gram	20.99	+0.01
BaCl <sub>2</sub> , 2.5 N (no NaCl)	20.94	-0.04
BaCl <sub>2</sub> , 1.2 N (1.5 N NaCl)	20.99	+0.01
CaCl <sub>2</sub> , 2.5 N (no NaCl)	21.00	+0.02
Co <sup>++</sup> , 0.45 gram	20.99	+0.01
Cr <sup>+++</sup> , 0.39 gram	20.94	-0.04
Cu <sup>++</sup> , 0.4 gram	21.01	+0.03
Mg <sup>++</sup> , 0.3 gram	20.99	+0.01
Mn <sup>++</sup> , 0.55 gram	21.00	+0.02
NH <sub>4</sub> Cl, 2.5 M (no NaCl)	20.92	-0.06
NH <sub>4</sub> Cl, 1.2 M (2.0 M NaCl)	20.94	-0.04
Ni <sup>++</sup> , 0.42 gram	20.98	0.00
Pb <sup>++</sup> , 0.55 gram	20.86	-0.12
H <sub>2</sub> SO <sub>4</sub> , 2 ml. (no HCl)		
Th <sup>++++</sup> , 0.66 gram	20.99	+0.01
UO <sub>2</sub> <sup>++</sup> , 0.64 gram	No excess reagent left	
Zr <sup>++++</sup> , 0.4 gram	20.94	-0.04

It was found that the tin could be determined by titrating the tetraphenylarsonium ion in the precipitate. The precipitate, after being filtered and washed as usual, was dissolved in hot water and the titration made potentiometrically with standard iodine (2). The solution was allowed to cool to room temperature before the end point was reached and was

not saturated with sodium chloride until that time, to avoid precipitating the tin compound again. Considerable tin was required to effect complete solution, but the addition of a few milliliters of ammonium hydroxide aids this process. When solution is complete this solution is made neutral or very slightly acidic.

TABLE VI. DETERMINATION OF TIN BY DIRECT TITRATION OF PRECIPITATE

Indirect Titration Mg.	Direct Titration Mg.	Error Mg.
7.80	7.73	-0.07
19.19	19.12	-0.07
19.50	19.55	+0.05
19.57	19.63	+0.06
19.62	19.64	+0.02
19.64	19.72	+0.08
19.74	19.83	+0.09

The accuracy is almost equal to that of the parallel indirect determination, as Table VI shows, but the latter method is preferred in general because of the time required to effect solution, and the much larger volume of iodine required in the direct titration. This large quantity of iodine forms a very bulky periodide precipitate which reduces the sensitivity of the reaction near the end point. The method might be employed profitably for less than 10 mg. of tin.

### Determination of Cadmium and Zinc

Cadmium and zinc may be determined with tetraphenylarsonium chloride by procedures similar to those for mercury and tin. In highly concentrated chloride solutions the complex chloride ions of cadmium,  $\text{CdCl}_4^{--}$ , and zinc,  $\text{ZnCl}_4^{--}$ , form insoluble white crystalline precipitates of tetraphenylarsonium chlorocadmiate,  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{CdCl}_4$ , and tetraphenylarsonium chlorozincate,  $[(\text{C}_6\text{H}_5)_4\text{As}]_2\text{ZnCl}_4$ , respectively. The precipitation is quantitative in the proper sodium chloride concentration if a sufficient excess of reagent is used, but the compounds are soluble in water. The chlorocadmiate precipitate is slightly more soluble than the corresponding chlorostannate precipitate and considerably more soluble than the chloromercuriate compound. This is indicated by the sodium chloride concentration required to cause complete precipitation. The chlorozincate compound is even more soluble. Because of this rather high solubility the determinations are, in general, subject to more interferences than the others.

The determinations were carried out, as usual, by titrating the excess of tetraphenylarsonium ion potentiometrically with iodine, using 0.015 to 0.020 M tetraphenylarsonium chloride and titrating with 0.020 to 0.025 N iodine solution containing 6 to 10 grams of potassium iodide per liter. The calculations of the quantities of cadmium or zinc are made in the usual way. One milliliter of 0.01 M tetraphenylarsonium chloride is equivalent to 0.5621 and 0.3269 mg. of cadmium and zinc, respectively. Solutions made from pure metals of cadmium and zinc were used in this work.

Since rather high sodium chloride concentrations (2.5 to 3.5 M) must be used, a limited excess of tetraphenylarsonium chloride must be used because of its slight solubility in high chloride concentrations. The permissible excess may be somewhat larger in highly acid solutions. Attempts to find an indicator for an excess of reagent were unsuccessful. Therefore it is necessary to run a trial determination to determine the approximate quantity of metal present.

On account of the solubility of these precipitates in water it seems certain that they could be dissolved and titrated directly with iodine, as in the case of tin, although this was not done.



TABLE VII. EFFECT OF VARIOUS IONS ON DETERMINATION OF CADMIUM

(Volume, 60 ml.; HCl, 0.3 M. Precipitates stood one hour. Cadmium present, 23.00 mg.; theoretical excess of reagent, 8.72 ml.)		
NaCl, M	Substances Present	Cadmium Error Mg.
3.0	NH <sub>4</sub> NO <sub>3</sub> , 1 gram	+0.10
3.2	NH <sub>4</sub> NO <sub>3</sub> , 1 gram	+0.19
3.2	NH <sub>4</sub> NO <sub>3</sub> , 0.5 gram	-0.02
3.0	K <sub>2</sub> SO <sub>4</sub> , 5 grams	+2.07
3.2	K <sub>2</sub> SO <sub>4</sub> , 1 gram	-0.01
3.0	Borax, 1 gram	+0.04
3.3	Borax, 1 gram	+0.01
3.3	Disodium phosphate, 1 gram	-0.05
3.3	Sodium acetate, 1 gram	+0.03
3.3	Sodium formate, 1 gram	+0.25
3.3	Ammonium tartrate, 1 gram	-0.07
3.3	Sodium citrate, 1 gram	+0.08
None	Ammonium chloride, 3.3 M	-0.25
None	Ammonium chloride, 3.7 M	-0.03
None	Potassium chloride, 3.3 M	+0.07
None	Calcium chloride, 1.7 M	-0.03
None	Barium chloride, 1.5 M	+0.08
2.8	Ni <sup>++</sup> , 223 mg.	+0.10
3.0	Mg <sup>++</sup> , 120 mg.	+0.05
3.0	Al <sup>+++</sup> , 150 mg.	+0.09
3.0	Co <sup>++</sup> , 248 mg.	+0.75
3.0	Co <sup>++</sup> , 248 mg.	+0.11
	Ammonium tartrate, 2 grams	
2.8	Ni <sup>++</sup> , 223 mg.	+0.06
	Ammonium tartrate, 2 grams	
2.8	Cr <sup>+++</sup> , 100 mg.	+0.07
3.0	Cu <sup>++</sup> , 255 mg.	+3.07
3.0	Cu <sup>++</sup> , 255 mg.	+0.09
	Sodium citrate, 2 grams	
2.8	Mn <sup>++</sup> , 277 mg.	+0.70
2.8	Mn <sup>++</sup> , 277 mg.	+0.04
	Ammonium tartrate, 4 grams	
3.0	Fe <sup>+++</sup> , 103 mg.	+0.76
	Sodium phosphate, 2 grams	
	Phosphoric acid, 2 ml.	
2.7	Fe <sup>+++</sup> , 103 mg.	+0.23
	Sodium phosphate, 2 grams	
	Phosphoric acid, 2 ml.	
2.0	Fe <sup>+++</sup> , 103 mg.	+0.12
	Sodium phosphate, 2 grams	
	Phosphoric acid, 2 ml.	
2.5	Pb <sup>++</sup> , 273 mg.	-0.06
	H <sub>2</sub> SO <sub>4</sub> , 3 ml.	
2.7	Sn <sup>++++</sup> , 22.5 mg.	-0.05
	Ammonium tartrate, 2 grams	
3.0	Sn <sup>++++</sup> , 45 mg.	+0.04
	Ammonium tartrate, 2 grams	

TABLE VIII. EFFECT OF VARIOUS IONS ON DETERMINATION OF ZINC

(Volume, 60 ml.; HCl, 0.3 M; precipitates stood 1 to 2 hours. Zinc, 15.40 mg.; theoretical excess of reagent, 9.70 ml., 0.015 M)		
NaCl, M	Substances Present	Zinc Error Mg.
3.0	NH <sub>4</sub> NO <sub>3</sub> , 1 gram	-0.07
3.0	K <sub>2</sub> SO <sub>4</sub> , 1 gram	-0.07
3.2	Borax, 1 gram	-0.04
3.0	Disodium phosphate, 1 gram	-0.03
3.5	Sodium acetate, 1 gram	+0.06
3.0	Sodium acetate, 1 gram	-0.04
3.0	Sodium formate, 1 gram	-0.07
3.0	Sodium citrate, 1 gram	-0.10
2.7	Sodium citrate, 4 grams	+0.12
	Citric acid, 2 grams	
3.3	Ammonium tartrate, 1 gram	-0.03
3.0	Ammonium tartrate, 1 gram	-0.09
None	Ammonium chloride, 3.7 M	-0.05
None	Potassium chloride, 3.5 M	+0.01
None	Calcium chloride, 1.8 M	-0.06
None	Barium chloride, 1.5 M	-0.04
3.0	Ni <sup>++</sup> , 223 mg.	+0.11
2.8	Ni <sup>++</sup> , 223 mg.	+0.05
	Ammonium tartrate, 2 grams	
3.0	Mg <sup>++</sup> , 120 mg.	-0.08
3.0	Al <sup>+++</sup> , 150 mg.	+0.03
2.8	Cr <sup>+++</sup> , 160 mg.	-0.01
2.8	Co <sup>++</sup> , 124 mg.	+0.04
2.8	Co <sup>++</sup> , 248 mg.	+0.55
2.8	Co <sup>++</sup> , 248 mg.	+0.06
	Ammonium tartrate, 2 grams	
2.8	Co <sup>++</sup> , 248 mg.	+0.04
	Sodium citrate, 3 grams	
2.8	Cu <sup>++</sup> , 128 mg.	-0.08
2.8	Cu <sup>++</sup> , 255 mg.	+1.89
2.8	Cu <sup>++</sup> , 255 mg.	+0.15
	Sodium citrate, 3 grams	
2.8	Mn <sup>++</sup> , 277 mg.	+0.40
2.8	Mn <sup>++</sup> , 277 mg.	+0.04
	Ammonium tartrate, 4 grams	
2.8	Mn <sup>++</sup> , 277 mg.	-0.07
	Sodium acetate, 4 grams	
2.8	Mn <sup>++</sup> , 277 mg.	+0.07
	Sodium phosphate, 4 grams	
2.5	Fe <sup>+++</sup> , 103 mg.	+0.15
	Sodium phosphate, 4 grams	
	H <sub>2</sub> PO <sub>4</sub> , 1.5 ml.	
2.8	Pb <sup>++</sup> , 273 mg.	+0.09
	H <sub>2</sub> SO <sub>4</sub> , 3 ml.	
2.8	Sn <sup>++++</sup> , 45 mg.	-0.03
	Ammonium tartrate, 2 grams	

PROCEDURE FOR DETERMINATION OF CADMIUM. The acidity of the cadmium solution, in as small volume as possible, is so adjusted that the hydrochloric acid concentration will be about 0.4 N in a final volume of 60 ml. Sufficient commercial (non-oxidized) sodium chloride is added to make a 3.0 to 3.5 M solution. An excess of standard tetraphenylarsonium chloride solution is added, and the mixture is diluted to 60 ml., stirred vigorously, and allowed to stand about an hour before filtering through a sintered glass crucible. The lower concentration of sodium chloride is not, and it may be reduced to 2.5 M if the concentration of other ions is high. The excess of reagent in 3.0 M sodium chloride solution should not exceed that amount which can remain dissolved in this volume—i. e., about 9 to 10 ml. of 0.015 M reagent in 3.0 M sodium chloride solution. The precipitate is filtered and washed with a saturated sodium chloride solution. The solution and washings are titrated potentiometrically with standard iodine in the usual way, to obtain by difference the volume of reagent required to precipitate the cadmium. A series of determinations showed that quantities of cadmium varying from 0.4 to 65 mg. in pure solutions could be determined with an error of  $\pm 0.09$  mg. but the excess of reagent was more critical than in the case of mercury and tin. It appeared probable that larger amounts could be determined. The best sodium chloride concentration is 3.0 to 3.5 M. At lower concentrations precipitation is incomplete, and at higher concentrations the reagent is likely to contaminate the precipitate. The best results are obtained in solutions with acidity varying from faintly acid to 0.4 M in hydrochloric acid. Nitric acid precipitates tetraphenylarsonium nitrate and also interferes with the subsequent titration. Organic acids interfere in some cases by forming complexes with the cadmium which hinder precipitation.

INTERFERING SUBSTANCES. Cadmium is subject to the same interferences as mercury and tin. Because of the higher concentrations of sodium chloride and the ability of cadmium to form complexes with certain organic acids, some ions interfere that do not interfere with mercury or even with tin. These include cupric, cobaltous, manganous, and ferric ions. It is possible to avoid interference by these ions when they are present in smaller quantities than those shown in the cases of mercury and tin. Those ions that form rather stable chloride complexes, such as mercuric, stannic, auric, platinic, zinc, ferric, cupric, cobaltous, and manganous ions interfere, as do such anions as the halides (other than chloride), thiocyanate, perchlorate, periodate, perrhenate, permanganate, nitrate, and those ions that are capable of oxidizing or reducing the iodine solution. Table VII shows the effect of the presence of certain ions and how certain interferences may be avoided. The phosphates and tartrates yield copious precipitates with the above metals and cause some of the tetraphenylarsonium to be salted out if the solution stands too long. In the case of cupric ion the citrate and acid must be added before the precipitation is made. Interference by small amounts of stannic ion may be avoided by the addition of tartrate ion. PROCEDURE FOR DETERMINATION OF ZINC. The procedure is identical with that for cadmium, except that the sodium chloride concentration should be nearer 3.5 M than 3.0 M for best results. Fairly satisfactory results may be obtained in 3.0 M sodium chloride if the maximum excess of reagent is used and the mixture allowed to stand about 3 hours before filtering.



Although solid tetraphenylarsonium chloride precipitates rather slowly in 3.0 to 3.5 *M* sodium chloride solutions, it is best to use no larger excess than can remain in solution in the aqueous sodium chloride—i. e., about 9 ml. of 0.015 *M* reagent in 3.5 *M* sodium chloride. With 4.0 *M* sodium chloride good results are obtained, but the excess of reagent is rather critical. With more than 45 mg. of zinc the precipitate becomes inconveniently bulky, and with less than 0.3 mg. the solubility error is too great and the time required is too long. The error in a series of experiments on pure solutions was  $\pm 0.09$  mg.

The acid concentration supplied only by hydrochloric acid should not be greater than 0.4 *M*. If the solution is made about 0.3 *M* a slightly larger excess of reagent may be used safely and the precipitate allowed to stand longer before filtering. No zinc precipitates in alkaline solution.

**INTERFERING SUBSTANCES.** Zinc is subject to the same interferences as cadmium. These interferences may be aggravated somewhat by the higher sodium chloride concentration re-

quired to effect complete precipitation of the zinc complex. The means whereby, and the extent to which, interferences may be avoided are the same as for cadmium. If the concentration of other substances is unusually high the concentration of sodium chloride should be reduced to 2.5 to 3.0 *M* to avoid salting out the excess tetraphenylarsonium chloride. Interference by mercury and cadmium cannot be avoided to any extent, although interference by as much as 10 mg. of stannic ion may be eliminated by the addition of 2 to 3 grams of an alkali tartrate. Interference by manganese may be avoided by use of acetate, phosphate, or tartrate. (Table VII)

#### Literature Cited

- (1) Lamprey, H., thesis, University of Michigan, 1935.
- (2) Willard and Smith, *IND. ENG. CHEM., Anal. Ed.*, **11**, 186 (1938).

FROM a thesis presented by G. M. Smith to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of doctor of philosophy.

## Colorimetric Determination of Manganese with Periodate

### A Spectrophotometric Study

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A NUMBER of early investigators (2, 6, 10, 11) studied the reaction between manganous and periodate ions with more or less conflicting results, but Willard and Greathouse (15) were the first to use it as the basis of a colorimetric method for the quantitative determination of manganese. Their method depends upon the oxidation in acid solution of manganous salts to permanganate by potassium periodate and they state that it is free from all the faults of the other methods for manganese and yields results of a high degree of accuracy. More recently it has been successfully applied to water (1), to animal and vegetable tissues (4, 12, 13), and to salt solutions (3).

The purpose of the work described in this paper was to make a study of this method by means of the photoelectric recording spectrophotometer (9), with particular attention to the effect of other ions upon the color system. Similar studies of other colorimetric methods have recently been made (5, 7, 14, 16). The recording spectrophotometer is an ideal instrument for making such an investigation, because if two solutions give identical spectral transmission curves they will have the same color under any condition of illumination and to any observer. By such curves very small differences in color intensity and in hue can be detected.

#### Apparatus and Solutions

All spectrophotometric measurements in the present work were made with the instrument built for the Department of Chemistry of Purdue University by the General Electric Co. (8).

A stock solution of potassium permanganate containing approximately 10 mg. of manganese per ml. was made by dissolving the proper amount of the salt in redistilled water and making the volume up to 1 liter. After 4 days this solution was filtered through asbestos and standardized against ferrous ammonium sulfate of known iron content. A 100-ml. volume of this solution was accurately measured into a beaker, 25 ml. of concentrated

sulfuric acid and 6 grams of potassium metaperiodate were added and the solution was boiled for 2 minutes. After 15 minutes on the hot plate, the solution was cooled to room temperature, accurately diluted to 1 liter in a volumetric flask, thoroughly mixed and transferred to a brown, glass-stoppered bottle. Each milliliter contained 0.09865 mg. of manganese. Because of the presence of the periodate this solution was stable and could be used as a standard throughout the work.

Standard solutions of the metals were prepared from the nitrate or sulfate salts, while the sodium, potassium, or ammonium salts were used for the preparation of standard solutions of the anions. Redistilled water was used throughout. Each milliliter contained 10 mg. of the ion in question. For the stannous, stannic, antimonous solutions it was necessary to evaporate a known volume of the chloride solution with concentrated sulfuric acid to remove all chloride and then make up to the original volume with dilute sulfuric acid. The resulting solutions gave negative chloride tests.

For producing the color system the procedure of Willard and Greathouse (15) was followed. To 5 ml. of the standard manganese solution, representing 0.4933 mg. of manganese, in a 250-ml. beaker about 25 ml. of water were added followed by 10 ml. of concentrated sulfuric acid, and the solution diluted to 100 ml. After the addition and solution of 0.3 g. of potassium metaperiodate, the solution was carefully boiled 1 minute, kept warm for 10 minutes, transferred to a 250-ml. volumetric flask, cooled to room temperature, made up to the mark, and thoroughly mixed.

The spectral transmission curves were determined for a solution of thickness of 4.983 cm. The absorption of the glass cell was compensated for by placing in the rear beam of light a similar cell filled with redistilled water.

The transmittancy curves for varying amounts of manganese are shown in Figure 1. The peak of the absorption band is located at 522  $m\mu$ .

#### Conformity to Beer's Law

That the color system follows Beer's law, at least up to a concentration of 20 mg. of manganese per liter, is apparent from Table I, in which are shown the observed transmittancy at 522  $m\mu$ , the wave length of maximum absorption, for



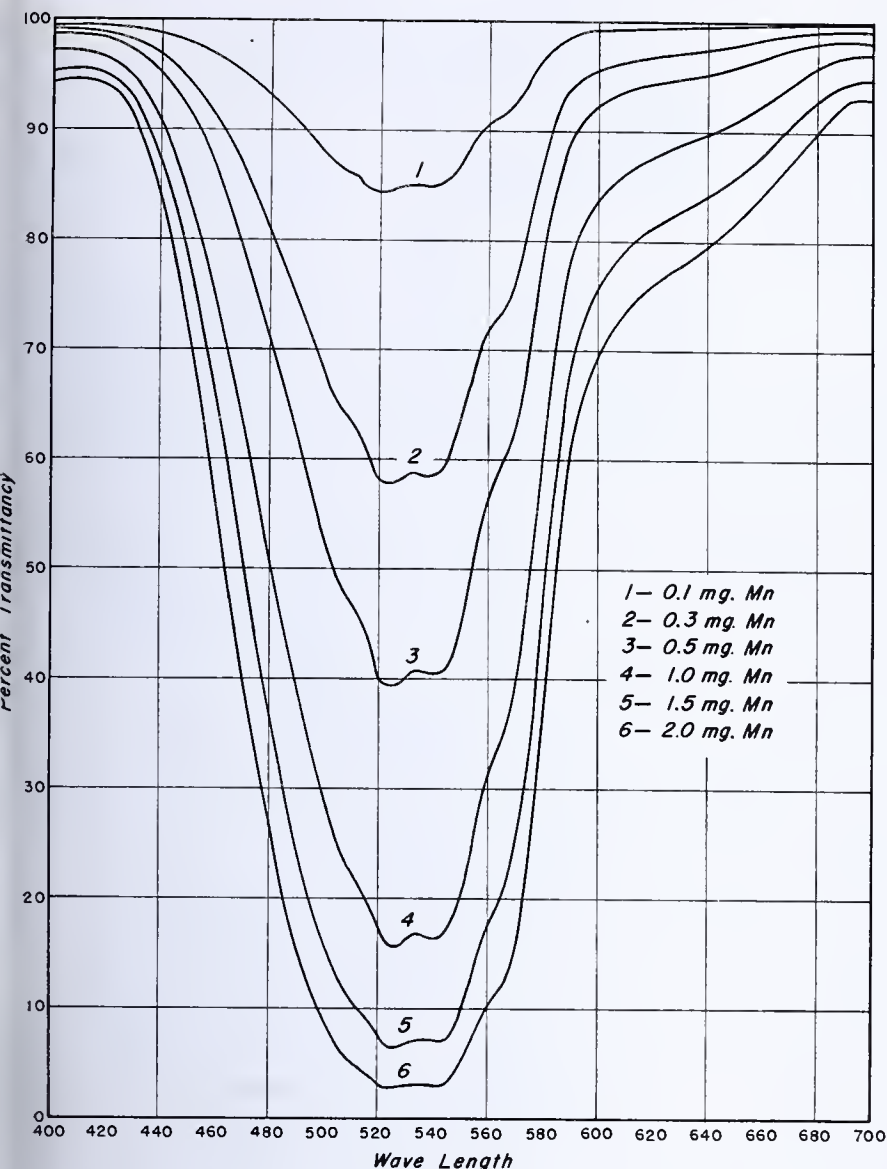


FIGURE 1. TRANSMITTANCY CURVES FOR MANGANESE

manganese solutions of different concentrations, together with the transmittancies, calculated by means of a special color slide rule from the transmittancy of the solution containing 5 mg. of manganese per liter. The calculations were made by use of the formula which expresses Beer's law

$$T_2 = T_1^{c_2/c_1}$$

where  $T_1$  represents the observed transmittancy, expressed as a decimal, for the solution of concentration  $c_1$ , and  $T_2$  the calculated transmittancy for the solution of concentration  $c_2$ . The observed and calculated values check satisfactorily.

TABLE I. VALIDITY OF BEER'S LAW

(1.961-cm. cell)					
Manganese Mg./l.	Transmittancy at 522 mμ		Manganese Mg./l.	Transmittancy at 552 mμ	
	Observed %	Calculated %		Observed %	Calculated %
1	84.7	84.5	10	18.4	18.4
3	60.2	60.2	15	7.7	7.9
5	43.0	..	20	3.7	3.4

Additional evidence that Beer's law is followed is given by the fact that a straight line results when the logarithm of the observed transmittancy is plotted against the concentration. Concentrations above 20 mg. per liter give solutions too deeply colored for visual determination.

### Effect of Reagents

Willard and Greathouse (15) state that the success of the reaction depends upon the presence of a sufficient concentra-

tion of acid to prevent the precipitation of manganic periodate or oxide and that the minimum concentration of acid required increases with the concentration of manganese. A number of metals, such as silver, lead, bismuth, and mercury, form iodates or periodates which are insoluble in dilute acids, but soluble in high concentration of acids. Because of the high concentration of acid needed, the pH values of the various solutions were so low—less than 1.0—that no attempt was made to determine them.

In studying the possible effect on the color of the amount and kind of acid present, the curve produced by the solution containing 5 ml. of the standard manganese solution (representing 0.4933 mg. of manganese), 10 ml. of concentrated sulfuric acid, and 0.3 gram of potassium periodate per 250 ml. was compared with the curves produced by a series of similar manganese solutions containing in place of the 10 ml. of sulfuric acid 15, 20, 25, and 30 ml. of concentrated sulfuric acid, 20, 30, and 40 ml. of concentrated nitric acid which had been decolorized by drawing air through it by suction, and 5, 10, 15, 30, and 50 ml. of concentrated phosphoric acid, respectively. From the transmittancies at 522 mμ of the standard solution and each of the other solutions and from the known manganese concentration of the standard solution, by use of the formula employed above in the Beer's law calculations, the apparent concentration of manganese in each of the other solutions was calculated by the aid of the special color slide rule. The difference between this value and the actual concentration multiplied by 100 and divided by the actual concentration gave the percentage error.

In accordance with the procedure of a former study (7) a 2 per cent error was arbitrarily set as the maximum allowable for negligible interference. Although visual methods of color comparison often have a precision of not less than 5 per cent, it was thought advisable to set a lower figure to provide for other possible factors. In all cases the curves were practically identical and the error was negligible except for the solutions containing 30 and 40 ml. of nitric acid, where it amounted to -4.0 and -5.0 per cent, respectively. Possibly these large amounts of nitric acid produced enough nitrogen oxides during the boiling and digestion to influence the color.

Varying the amount of potassium periodate added has no appreciable effect upon the color. Curves for a series of solutions containing in 250 ml. 0.4933 mg. of manganese and 10 ml. of concentrated sulfuric acid with 0.2, 0.4, 0.5, and 0.6 gram of potassium periodate, respectively, showed a negligible error when compared to the standard curve made from the solution containing 0.3 gram of potassium periodate. Therefore it is possible to add an excess of periodate when reducing agents are present and thus prevent reduction of the permanganate and consequent fading of the color of the solution.

### Stability of the Color

Because of the presence of periodate in the solution there is practically no tendency of the color to fade on standing. Willard and Greathouse (15) found it stable for 3 months when measured by a visual colorimeter and Clark (3) reported it stable for 7 months.



Curves made at intervals for six solutions containing, respectively, 0.25, 0.75, 1.25, 2.5, 3.75, and 5.0 mg. of manganese with 10 ml. of concentrated sulfuric acid and 0.3 gram of potassium periodate per 250 ml., after the solutions had stood in glass-stoppered Pyrex bottles in diffuse light, gave no evidence whatever of fading or other change in the color over a period of 2 months. Lack of time prevented tests over any longer period. Such marked stability makes possible the use of a series of permanent standards.

Effect of Anions

In the ion interference studies the curve produced by the standard manganese solution, containing 0.4933 mg. of manganese, 10 ml. of concentrated sulfuric acid, and 0.3 gram of periodate per 250 ml., was compared with the curve produced by a similar manganese solution containing a known amount of the added ion. Calculations of the percentage error were made as explained above.

A considerable number of the common anions, cyanide, thiocyanate, iodide, bromide, chloride, oxalate, tartrate, citrate, sulfite, nitrite, and arsenite, have the ability to reduce the permanganate and thus decrease the color intensity. However, by using larger amounts of periodate this reducing action may be prevented for moderate amounts of the ions and the permanganate may be kept in the oxidized state with the color unchanged. In the usual procedure for determining manganese these reducing ions will be removed during the boiling with nitric acid and the subsequent evaporation with sulfuric acid. In general it is preferable to remove them.

In Figure 2, curve 4 shows the effect of 10 mg. of oxalate per 250 ml., curve 5 the effect of 3 mg. of nitrite per 250 ml., and curve 6 the effect of 50 mg. of sulfite per 250 ml. In each case 0.3 gram of periodate was used. Certain colored ions, as dichromate, cause a change in hue. In Figure 2, curves 2 and 3 show the respective effects of 10 and 2.5 mg. of dichromate per 250 ml. Thiosulfate

in addition to its reducing action also causes the precipitation of sulfur in the acid solution. Tungstate causes turbidity because of the precipitation of tungstic acid in the acid solution.

The effects of the common anions and their approximate limiting concentrations are listed in Table II.

Effect of Cations

In the tests involving barium, calcium, lead, and strontium ions it was necessary to substitute concentrated phosphoric acid for the sulfuric acid, and a standard permanganate solution to which no sulfuric acid had been added was used. In each case except for lead, where 10 ml. of phosphoric acid were necessary to prevent precipitation, 5 ml. sufficed.

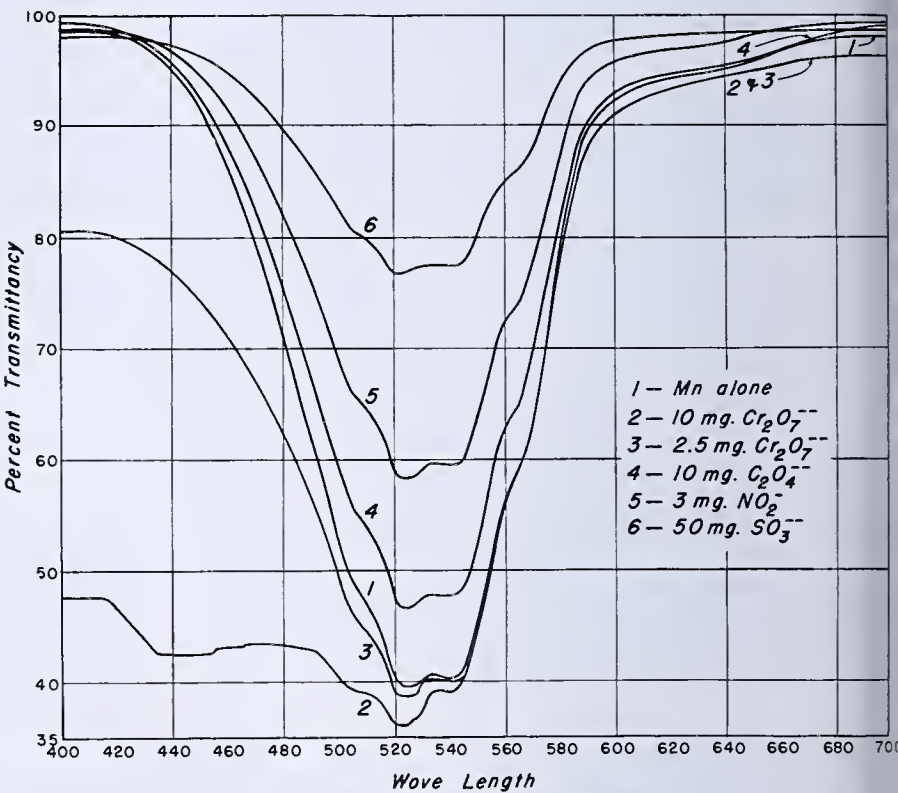


FIGURE 2. EFFECT OF ANIONS

0.4933 mg. of manganese, diverse ion, 10 ml. of concentrated sulfuric acid, and 0.3 gram of potassium iodate in 250 ml. of solution. 4.983-cm. cell

TABLE II. EFFECT OF COMMON ANIONS ON THE COLOR DEVELOPED BY MANGANESE  
(0.4933 mg. of manganese in 250 ml. of solution)

Anion				Cation			
Ion		Concentration		Ion		Concentration	
		Mg./250 ml.				Mg./250 ml.	
		Apparent Change in Manganese Concentration %				Apparent Change in Manganese Concentration %	
		Limiting Concentration Mg./250 ml.				Limiting Concentration Mg./250 ml.	
Acetate	60	Negligible	..	Nitrite	50	Decolorized	..
Arsenate	100 (As)	Negligible	..		50 (0.6 gram KIO <sub>4</sub> )	- 5.9	..
Arsenite	50 (As)	Change in hue	..		10	Decolorized	..
	20 (As)	-63.7	..		10 (0.6 gram KIO <sub>4</sub> )	- 4.4	..
	10 (As)	-36.1	0.0		3	-43.6	0.0
Borate	150 (B <sub>2</sub> O <sub>3</sub> )	Negligible	..	Orthophosphate	200 (P <sub>2</sub> O <sub>5</sub> )	Negligible	..
Bromide	50	-7.0	10	Oxalate	50	Decolorized	..
	50 (0.6 gram KIO <sub>4</sub> )	Negligible	50		50 (0.6 gram KIO <sub>4</sub> )	Decolorized	..
Carbonate	200	Negligible	..		10	-18.0	0.0
Chlorate	100	Negligible	..		10 (0.6 gram KIO <sub>4</sub> )	Negligible	10
Chloride	100	-35.0	..	Perchlorate	100	Negligible	..
	50	- 3.0	30	Pyrophosphate	200 (P <sub>2</sub> O <sub>5</sub> )	Negligible	..
Citrate	50	Decolorized	..	Silicate	100 (SiO <sub>2</sub> )	Negligible	..
	50 (0.6 gram KIO <sub>4</sub> )	Decolorized	..	Sulfate	300	Negligible	..
	10	- 2.6	7	Sulfite	50	-71.6	..
Cyanide	100	-10.0	..		10	-12.5	0.0
	50	- 3.5	25		10 (0.6 gram KIO <sub>4</sub> )	- 3.6	3
Dichromate	10	Change in hue	..	Tartrate	50	Decolorized	..
	2.5	Change in hue	0.0		50 (0.6 gram KIO <sub>4</sub> )	- 3.1	25
Fluoride	50	Negligible	..		10	- 2.0	10
Iodide	50 (0.6 gram KIO <sub>4</sub> )	Negligible	50	Thiocyanate	100	Change in hue	..
	10	- 5.0	3		100 (0.6 gram KIO <sub>4</sub> )	- 6.2	10
Molybdate	10 (Mo)	- 3.4	5		50	- 5.6	25
Nitrate	200	Negligible	..	Thiosulfate	1	Turbidity	0.0
				Tungstate	30	Precipitates	..
					10	Precipitates	0.0



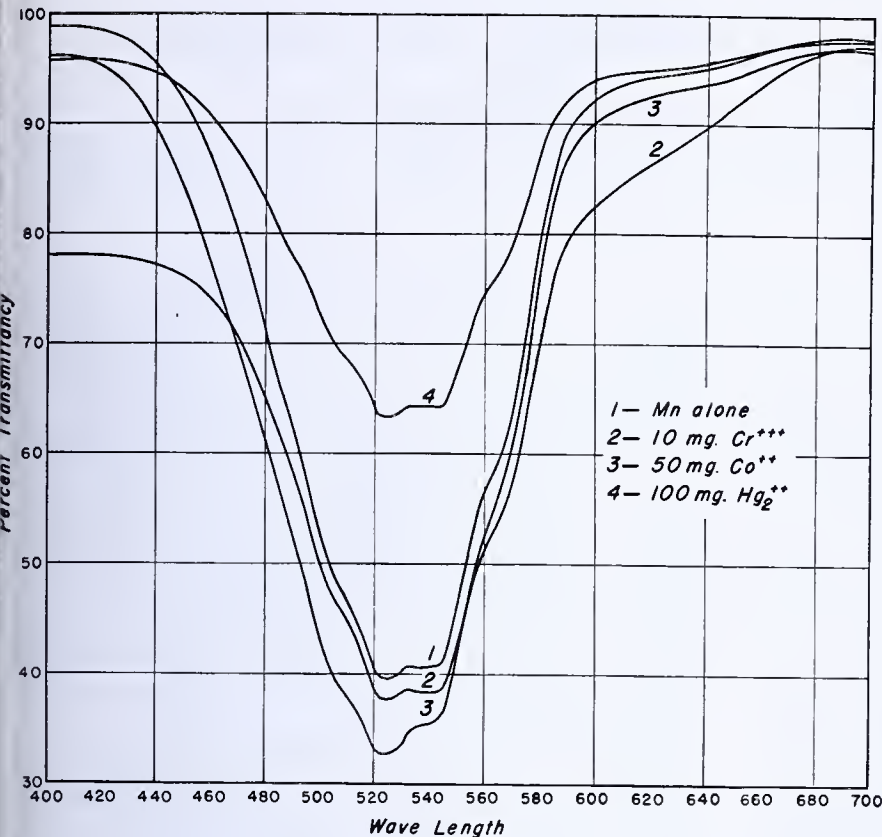


FIGURE 3. EFFECT OF CATIONS  
4.933 mg. of manganese, diverse ion, 10 ml. of concentrated sulfuric acid, and 0.3 gram of potassium periodate in 250 ml. of solution. 4.983-cm. cell

The most common interference caused by cations is due to those which impart a color of their own to the solution and thereby cause a change in hue. Examples are cupric, nickelous, cobaltous, chromic, uranyl, and ferric ions (Figure 3, curves 2 and 3). The color caused by ferric ion may be removed by the addition of sufficient phosphoric acid to form the colorless complex ion. The curve then coincides with the standard curve. Willard and Greathouse (15) suggest correct-

ing for the color imparted by these colored cations by adding the same amounts to the color standard as are present in the sample. Silver, lead, and mercuric ions form iodates or periodates which are insoluble in dilute acids, but dissolve in high concentrations of acids. Bismuth and stannous ions give turbidity even in strongly acid solution and should be removed. Although antimonous ion readily reduces permanganate, the amount of the former left in solution after evaporation with sulfuric acid is so small that the periodate will easily oxidize it and prevent any reduction of the permanganate. Because of its reducing action mercurous ion causes a decrease in the color intensity (Figure 3, curve 4). Ferrous ion reduces the periodate to free iodine which colors the solution and causes a change in hue. It should, therefore, be oxidized by boiling with nitric acid.

In Table III are listed the effects of the common cations and their approximate limiting concentrations.

Summary

A spectrophotometric study shows that the periodate method for the determination of manganese colorimetrically is a most satisfactory one with very few limitations.

Sulfuric, nitric, or phosphoric acid may be present in widely varying amounts. A large excess of periodate may be used without interfering with the color.

The color system follows Beer's law. The color is stable in diffuse light for at least 2 months.

A study of the effect of fifty-six of the common ions was made. A few seriously interfere with the color, but in the course of the determination most of these would be removed.

Acknowledgments

The writer wishes to express his sincere appreciation to M. G. Mellon of Purdue University, in whose laboratory this investigation was conducted, and to thank him for the privilege of using the Purdue spectrophotometer. Thanks are also given to J. T. Woods and D. H. Byers for their aid in adjusting the spectrophotometer.

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TABLE III. EFFECT OF COMMON CATIONS ON THE COLOR DEVELOPED BY MANGANESE			
(0.4933 mg. of manganese in 250 ml. of solution)			
Ion	Concentration	Apparent Change	Approximate
	Mg./250 ml.	in Manganese Concentration %	Limiting Concentration Mg./250 ml.
Aluminum	100	Negligible	..
Ammonium	100	Negligible	..
Antimonous	100	Negligible	..
Barium	100	Negligible	..
Beryllium	50	Negligible	..
Bismuth	50 (20 ml. H <sub>2</sub> SO <sub>4</sub> )	Turbidity	0.0
Cadmium	100	Negligible	..
Calcium	100	Negligible	..
Chromic	50	Change in hue	..
	10	Change in hue	0.0
Cobaltous	50	+18.1	..
	10	+ 3.0	5
Cupric	50	Change in hue	..
	10	Change in hue	5
Ferric	100 (10 ml. H <sub>3</sub> PO <sub>4</sub> )	Negligible	..
Ferrous	5	Change in hue	0.0
Lead	100 (10 ml. H <sub>3</sub> PO <sub>4</sub> )	Negligible	..
Lithium	100	Negligible	..
Magnesium	100	Negligible	..
Mercuric	100 (20 ml. H <sub>2</sub> SO <sub>4</sub> )	Negligible	..
Mercurous	100	-50.7	..
	50	- 1.1	50
Nickelous	50	Change in hue	..
	10	Negligible	10
Potassium	125	Negligible	..
Silver	100 (20 ml. H <sub>2</sub> SO <sub>4</sub> )	Negligible	..
Sodium	155	Negligible	..
Tannic	50	Negligible	..
Tannous	20 (20 ml. H <sub>2</sub> SO <sub>4</sub> )	Turbidity	0.0
Thorium	100	Negligible	..
Thorium	100	Negligible	..
Uranyl	50 (U)	- 2.0	50
Zinc	100	Negligible	..
Zirconium	100	Negligible	..



# Separation and Determination of Aluminum and Beryllium Using Tannin

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## Chemicals and Apparatus

SINCE the chemical properties of aluminum and beryllium and their compounds are very similar, and because aluminum occurs in many of the ores of beryllium, most methods for the analysis of beryllium take into account the preliminary separation of aluminum. These include the bicarbonate method (15), the method employing hydrochloric acid gas and a cold solution of the chlorides of aluminum and beryllium in equal parts of hydrochloric acid and ether (6), the use of tannin (12), and the most recent method proposed by Kolthoff and Sandell (9) and modified by Knowles (7) in which 8-hydroxyquinoline is used to precipitate and remove the aluminum.

The use of tannin in analytical chemistry arises from the fact that a solution of common tannin or gallotannic acid ( $C_{14}H_{10}O_9 \cdot 2H_2O$ ) is essentially a colloidal suspension of negatively charged particles capable of flocculating the positively charged particles of certain inorganic compounds such as the hydrous oxide sols. In 1925 Powell and Schoeller (16) recommended the use of tannin for the separation of tantalum from columbium. Their co-workers (17) extended the use of this reagent to the determination of such elements as titanium, zirconium, and hafnium. In 1927 Moser and Niessner proposed a method (12) for the separation and determination of aluminum and beryllium using tannin, in which the aluminum is precipitated from a "weakly acid (acetic) or neutral solution" as the insoluble aluminum hydroxide tannin complex while the beryllium forms a "soluble complex salt" in the presence of tannin and ammonium acetate and remains in solution (13). In a later article on the separation of beryllium from other elements such as vanadium, tungsten, chromium, iron, etc., the acidity conditions are more definitely defined.

The difficulty with the procedures recommended by Moser, as evidenced by the opinion of other analysts who have attempted to apply the methods, lies in the fact that the acidity conditions are not specified accurately nor definitely and that there is not a large enough difference in acidity between the precipitation point of the beryllium tannin complex and the tannin complexes of some of the other metals to make clean-cut separations possible. Schoeller and Webb state (18) that "even simple acetate solutions present difficulties in this respect (adjustment of acidity) as in Moser and Niessner's proposed method for the separation of aluminum from beryllium." Mitchell and Ward found (11) that they "did not obtain satisfactory separations by the method of Moser and Niessner, possibly owing to the insufficiently definite specifications of the acidity conditions in their description." Dixon criticizes (5) Moser and Singer's method for the separation of iron from beryllium, stating that it is likely to lead to coprecipitation of beryllium with iron at the reduced acidity required for complete precipitation of the iron.

In the opinion of the authors there is no apparent reason why beryllium should form a soluble salt, but satisfactory separations of beryllium from aluminum or other elements using tannin should depend upon the accurate specification and adjustment of pH conditions.

Baker and Adamson's reagent grade aluminum sulfate octadecahydrate was recrystallized three times from distilled water containing a small amount of sulfuric acid. Pure beryllium carbonate, prepared in this laboratory, was acidified with sulfuric acid and the carbon dioxide expelled. The solid impurities were filtered off, and the beryllium sulfate tetrahydrate was recovered by evaporation and recrystallized twice from distilled water acidified with sulfuric acid. Solutions of these were prepared and found to contain no impurities when tested by spectroscopic methods. The solutions were standardized by precipitating hydroxides with ammonia (10) and igniting in platinum at 1200 to 1300° C. in a platinum-wound muffle furnace. The results of four determinations on each solution gave values of 2.464 ± 0.005 mg. of aluminum oxide per ml. and 3.790 ± 0.003 mg. of beryllium oxide per ml. The tannin and ammonium acetate gave no appreciable ash upon ignition.

All measurements of the hydrogen-ion concentration were made with a glass electrode (14), Leeds & Northrup Type potentiometer, and Type R No. E galvanometer, shielded with grounded copper case. An ultramicroscope was used to determine the presence or absence of colloidal material in the solutions.

## Experimental

In Moser's procedure (12) employing tannin to precipitate aluminum, the use of large amounts of ammonium acetate was recommended. To determine whether the ammonium acetate merely acted as a buffer or whether in some way it prevented the precipitation of the beryllium tannin complex, as stated by Moser, the effect of the acetate concentration on the precipitation of aluminum and beryllium hydroxides and the effect of the addition of tannin to such solutions at different pH values were investigated.

Solutions approximately 0.0014 *N* as regards the oxides were adjusted to a pH of 1 with sulfuric acid and a saturated solution of ammonium acetate was added until the ammonium acetate concentration reached 1 *N*—the concentration used by Moser. Then (1 to 1) ammonium hydroxide was added to increase the pH and the solutions were examined at room temperature for the appearance of precipitates. They were then heated for several hours at 85° C. and re-examined for precipitate formation. To these solutions tannin was added, and, upon boiling for a few minutes, the presence of a tannin complex was determined.

The results (Tables I and II) show that the addition of ammonium acetate raises the precipitation pH of the solutions.

TABLE I. PRECIPITATION OF ALUMINUM

Sample No.	pH at 25° C.	Total Saturated $NH_4OAc$ Added <i>Ml.</i>	Total 1 to 1 $NH_4OH$ Added <i>Ml.</i>	Visible $Al(OH)_3$ Precipitation at 25° C.	$Al(OH)_3$ Precipitation after Heating 2 Hours at 85° C.	Al-Tan Precipitate on Heating to Boil
1	1.00	0	None	None	None	None
2	1.41	5	None	None	None	None
3	3.39	10	None	None	None	Heavy
4	4.28	15	None	None	5+	Heavy
5	4.57	20	None	None	3+	Heavy
6	4.74	25	None	None	2+	Heavy
7	4.92	35	None	None	1+	Heavy
8	4.96	37	None	Faint cloudiness	1+	Heavy
9	5.01	39	None	Cloudiness	1+	Heavy
10	5.08	45	None	Very faint precipitate	1+	Heavy
11	5.15	50	None	Very faint precipitate	1+	Heavy
12	5.33	50	5	Faint precipitate	1+	Heavy
13	7.73	50	20	Large precipitate	5+	Heavy



TABLE II. PRECIPITATION OF BERYLLIUM

Sample No.	pH at 25° C.	Total Saturated NH <sub>4</sub> OAc Added Ml.	Total 1 to 1 NH <sub>4</sub> OH Added Ml.	Visible Be(OH) <sub>2</sub> Precipitation at 25° C.	Visible Be(OH) <sub>2</sub> Precipitation on Heating 6 Hours at 85° C.	Be-Tannin Precipitation on Heating to Boiling
1	0.94	0	None	None	None	None
2	2.23	10	None	None	None	None
3	4.35	20	None	None	None	None
4	4.66	30	None	None	None	Very faint opalescence
5	4.86	40	None	None	None	Very faint opalescence
6	4.99	50	None	None	None	Faint opalescence
7	5.12	50	5.0	None	None	Opalescence
8	5.28	50	10.0	None	None	Faint precipitate
9	5.50	50	15.0	None	None	Precipitate, settled rapidly
10	5.86	50	20.0	None	None	Heavy precipitate
11	6.10	50	21.0	None	None	Heavy precipitate
12	6.31	50	21.2	None	None	Heavy precipitate
13	6.45	50	21.4	Very light precipitate	Very light precipitate	Heavy curdy precipitate
14	6.60	50	21.6	Light precipitate	Light precipitate	Heavy curdy precipitate
15	6.67	50	21.8	Precipitate	Precipitate	Heavy curdy precipitate
16	6.72	50	22.0	Precipitate	Precipitate	Heavy curdy precipitate
17	6.90	50	23.0	Precipitate	Precipitate	Heavy curdy precipitate
18	7.22	50	25.0	Precipitate	Precipitate	Heavy curdy precipitate
19	8.16	50	30.0	Precipitate	Precipitate	Heavy curdy precipitate

...ve that at which the hydroxides normally start to precipi-  
e in the cold. Britton found that aluminum hydroxide  
rmally precipitates in the cold at a pH of 4.1 (2) but in the  
esence of acetate no precipitation occurred until a pH of  
9 (4) was reached and with beryllium the precipitation in  
e presence of acetate occurred at a pH of 5.90 (4). He says  
that "even though pH values were established which were  
her than those at which aluminum hydroxide should pre-  
cipitate, the solution remained clear. It is likely that some  
rtion of the hydroxide was in the state of either a colloidal  
pseudocolloidal solution which was stabilized by some kind  
partial combination with acetic acid." In this case the  
ecipitation of the aluminum and beryllium hydroxides did  
t occur in the cold until pH values of 4.96 and 6.45 were  
ched, which is probably due to the fact that the authors'  
utions contained a much larger acetate ion-metal ion ratio  
n the solutions used by Britton.

Upon heating the solutions, aluminum hydroxide is precipi-  
ed, although in varying amounts, as soon as a pH greater  
an 4.1 is reached, while with beryllium hydroxide the value  
es not change. With aluminum the higher the acetate  
ncentration the less the amount of precipitate although the  
is raised. This was shown with sample 7, Table I, where  
on dilution with an equal volume of water and heating a  
uminous precipitate of aluminum hydroxide formed al-  
ough the change in pH in this well buffered solution was  
ligible. The aluminum solutions also showed "reversible  
hydrolysis" (1) as the precipitates formed in hot solution re-  
solved to some extent after the solutions were cooled. The  
ults with beryllium hydroxide seem to indicate that beryl-  
n forms a more stable complex with acetate than aluminum  
d is not so readily or completely hydrolyzed.

The addition of tannin to these solutions followed by boiling  
e heavy precipitates with aluminum in all cases where the  
was greater than 3.39 and a slight opalescence with beryl-  
n at a pH of 4.66 which increased as the pH was raised.  
the case of aluminum this would be expected, because of  
reciprocal flocculation of tannin and a metal hydroxide.  
en in those cases where no visible precipitate of aluminum  
droxide was shown, ultramicroscopic investigation and  
lysis experiments indicated that colloidal aluminum hy-  
oxide was present. In the case of beryllium the formation  
he tannin complex is not compatible with Moser's conten-  
a (12) that beryllium hydroxide forms a soluble complex  
h ammonium acetate and tannin and that freshly precipi-  
ed beryllium hydroxide is immediately dissolved and a

clear solution remains when it is treated with a 3 per cent tannin solution in saturated ammonium acetate. Attempts to reproduce this latter experiment always yielded the usual voluminous light yellow beryllium tannin complex.

Although the previous experiments indicated that the metal tannin complexes were formed through the mutual coagulation of the metal hydroxides by tannin, still there was a large difference in the pH at which the hydroxides precipitated at room temperature and when boiled with ammonium acetate and tannin—namely, with aluminum at pH 4.96 and 3.39 and with beryllium at pH 6.45 and 4.66.

To determine more accurately the pH at which incipient precipitation of the metal tannin complexes occurred, a mixture of 20 ml. of the solution of the pure metal sulfate, 25 ml. of saturated ammonium sulfate, and 50 ml. of 3 per cent tannin solution was diluted to 500 ml. and adjusted to a pH of 1 with sulfuric acid. The solution was heated to boiling and (1 to 1) ammonium hydroxide added dropwise until precipitation commenced. The solution was then cooled to room temperature and the

pH determined.

The pH values found for the precipitation of the tannin complexes were 3.04 for aluminum and 4.90 for beryllium. It is well known (8) that although  $pK_a$  changes with temperature, in acid solutions such as these the hydrogen-ion concentration remains practically constant. On this assumption a comparison of the pOH values at which the precipitation occurs, as given in Table III, shows that there is no great difference in these values at different temperatures.

TABLE III. pH AND pOH OF PRECIPITATION

	Al(OH) <sub>3</sub>			Be(OH) <sub>2</sub>		
	25° C.	100° C.	Diff.	25° C.	100° C.	Diff.
pH	4.96	3.04	1.92	6.45	4.90	1.55
pOH	9.04	9.16	0.12	7.55	7.30	0.25

The effect of pH, tannin concentration, and digestion time after the addition of the tannin on the completeness of the recovery of aluminum from solution were investigated by the following procedure:

A known amount of aluminum sulfate was added to 500 ml. of water, saturated ammonium acetate solution was added, and the pH was adjusted with 6 N sulfuric acid. The solution was heated to boiling, 3 per cent tannin solution was added, the heating was continued over a free flame for the short periods or on a steam bath for the longer time periods, and the solution was allowed to cool. The precipitate was filtered off in a Munroe crucible, washed with ammonium acetate tannin solution of the same pH as used in the precipitation, dried to constant weight at 110° C., weighed, ignited to aluminum oxide at 1200° to 1300° C., and weighed. The results are given in Table IV.

These experiments show that: (1) complete recovery of aluminum from solution is effected when the pH is  $4.6 \pm 0.1$  and the digestion time after the addition of the tannin is at least an hour. This length of time is necessary to complete the hydrolysis of the aluminum acetate and ensure complete precipitation of the aluminum tannin complex. (2) pH changes within the limits studied (samples, 3, 4, and 5) had no pronounced effect on the recovery of aluminum, although complete recovery was not secured in any of these cases since the digestion time was only 2 minutes. However, the pH should not rise above the point at which the beryllium tannin complex starts to precipitate—i. e., 4.9 at 100° C. (3) The amount of tannin used should be at least 12 to 15 times the weight of aluminum oxide determined, but greatly increasing



TABLE IV. EFFECT OF pH, TANNIN CONCENTRATION, AND DIGESTION TIME

Sample No.	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Saturated NH <sub>4</sub> OAc Added Ml.	pH	3% Tannin Solution Ml.	Digestion Time Min.	Al-T Complex Gram	Al <sub>2</sub> O <sub>3</sub> Recovered Gram	Tannin in Al-T Complex Gram	Al Recovered Mole	Tannin in Complex Mole	Moles Al Moles Tannin
1	0.0246	25	4.61	30	2	0.3862	0.0245	0.3617	0.00048	0.00112	0.43
2	0.0493	25	4.61	50	2	0.6023	0.0483	0.5540	0.00095	0.00172	0.55
3	0.0740	15	4.42	30	2	0.7545	0.0715	0.6830	0.00140	0.00212	0.66
4	0.0740	50	5.15	30	2	0.7952	0.0718	0.7234	0.00141	0.00224	0.63
5	0.0740	25	4.64	30	2	0.7087	0.0721	0.6366	0.00141	0.00198	0.71
6	0.0740	25	4.64	50	5	0.9770	0.0729	0.9041	0.00143	0.00281	0.51
7	0.0740	25	4.60	50	30	1.0874	0.0738	1.0136	0.00145	0.00315	0.46
8	0.0740	25	4.61	50	60	1.0440	0.0742	0.9698	0.00145	0.00301	0.48
9	0.0740	25	4.61	50	3.5 hours	1.1735	0.0739	1.0996	0.00145	0.00342	0.42
10	0.0740	25	4.62	50	5.5 hours	1.2579	0.0743	1.1836	0.00146	0.00368	0.40

the amount of excess tannin has no effect. (4) The dried precipitates do not suffer a constant percentage loss on ignition. Moser and Niessner (12) secured similar results which they interpreted as proof that a definite compound was not formed.

Since complete recovery of aluminum from solution was effected as outlined above, solutions of known aluminum-beryllium content were analyzed according to the following recommended procedure:

The solution containing the aluminum and beryllium is introduced into a large (800-ml.) beaker. If more than 0.08 gram of aluminum oxide or beryllium oxide is present, the tannin precipitates become too bulky and large to be handled conveniently. In this event, an aliquot of the sample is taken for analysis. Twenty-five milliliters of saturated ammonium acetate solution are added, the solution is diluted to 500 ml., and the pH is adjusted to about 4.6 with 6 *N* sulfuric acid and (1 to 1) ammonium hydroxide. After heating to boiling, 50 ml. of 3 per cent tannin solution, or at least 12 to 15 times the combined weight of beryllium oxide and aluminum oxide to be determined, are added slowly and the whole is digested on a steam bath for 1 hour.

The solution is allowed to cool to room temperature and the aluminum-tannin complex is filtered off on a coarse-textured quantitative filter paper. After thorough washing with a wash solution containing 5 per cent ammonium acetate and a little tannin and adjusted to pH 4.6, the precipitate is placed in a covered platinum crucible, carefully dried and ignited, and finally heated at 1200° to 1300° C. to constant weight. At these elevated temperatures, the loss in weight of the platinum crucibles must be taken into account.

The pH of the wash solution used on the aluminum tannin complex must be carefully adjusted, because if the pH is too high, beryllium-tannin complex might be precipitated on the surface of the aluminum tannin precipitate and thus make the results for aluminum too high and for beryllium too low. If the pH of the wash solution is below 4.1 it is possible that some of the aluminum tannin precipitate might dissolve and pass into the filtrate to be determined as beryllium.

The beryllium is determined in the filtrate by Moser's alternate procedure (13). Tannin equivalent to 10 to 12 times the weight of beryllium oxide to be determined is added in the form of a 3 per cent solution to the weakly acid filtrate and washings from the aluminum separation. After heating this solution to boiling, (1 to 1) ammonium hydroxide is added dropwise. A pale yellow precipitate of beryllium tannin complex forms as soon as the pOH reaches 7.3. In order to ensure complete precipitation which occurs at the isoelectric point of beryllium hydroxide, pH approximately 7.5 at room temperature (2), the addition of ammonium hydroxide is continued until the solution is just basic to litmus. The flame is then removed and the precipitate allowed to settle. It is not necessary to digest after the beryllium precipitation has taken place, since beryllium hydroxide is completely and practically instantaneously precipitated and removed by the tannin at the isoelectric point.

Care must be taken to have an excess of tannin present and to avoid a large excess of ammonia. In a hot, strongly basic solution tannin itself forms a gummy mass which adheres to the side of the beaker and coats the beryllium tannin precipitate. This makes it impossible to transfer the precipitate quantitatively from the beaker and to wash it free from impurities (18).

The precipitated beryllium tannin complex is filtered off on a coarse filter paper and washed with a 5 per cent ammonium acetate solution containing a little tannin and made just basic to litmus. The precipitate is dried and ignited to constant weight in a platinum crucible at 1200° to 1300° C.

The ignited precipitates of aluminum oxide and beryllium oxide should be white, indicating complete removal of organic matter. If the precipitates are not white, they are cautiously fumed once or twice with a few drops of nitric acid before the final ignition.

The results of determinations using the above procedure as given in Table V, show that satisfactory separations of aluminum from beryllium are obtained.

TABLE V. ANALYSIS OF KNOWN SOLUTIONS

Determination	Al <sub>2</sub> O <sub>3</sub> Taken Gram	Al <sub>2</sub> O <sub>3</sub> Recovered Gram	Error Mg.	BeO Taken Gram	BeO Recovered Gram	Error Mg.
1	0.0124	0.0128	+0.4	0.0266	0.0264	-0.2
2	0.0247	0.0250	+0.3	0.0266	0.0268	+0.2
3	0.0493	0.0496	+0.3	0.0265	0.0268	+0.3
4	0.0740	0.0742	+0.2	0.0532	0.0531	-0.1
5	0.0740	0.0742	+0.2	0.0797	0.0799	+0.2
6	0.0124	0.0126	+0.2	0.0797	0.0797	+0.0
7	0.0739	0.0739	+0.0	0.0114	0.0112	-0.2
8	0.0247	0.0250	+0.3	0.0266	0.0268	+0.2

Determination 8 was made in the presence of large amount of chloride ion, although Moser and Niessner state that presence of chloride ion causes premature precipitation of beryllium tannin complex and makes the separation of aluminum from beryllium impossible.

### Summary

Moser and Niessner's method for the separation and determination of aluminum and beryllium using tannin will give satisfactory results with careful regulation of the pH of solution and time of digestion.

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# Activated Sludge—Milorganite

## Constituents, Elements, and Growth-Producing Substances

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ACTIVATED sludge, produced at the Milwaukee Sewage Disposal Plant to the extent of approximately 110 metric tons per day and sold under the trade name of "Milorganite", has given excellent results as an ingredient of mixed fertilizers and as a direct fertilizer for lawns, golf course fairways, and certain special fruit and truck crops grown on sandy or other soils low in organic matter. Results of preliminary experiments relative to its fertilizer value were reported by Noer (1) in 1926. Although its nitrogen and available phosphoric acid contents of about 6 and 2.5 per cent, respectively, account for its main fertilizer value, the results obtained in practice seem to indicate appreciable benefits from other constituents. This has raised the question as to whether or not milorganite contains sufficient amounts of the minor nutrient elements and possibly plant hormones to promote plant growth in certain cases. In order to help answer this question, it was decided to make a rather extended analysis of milorganite, the results of which are here reported.

### Gross Composition

The main groups of organic compounds and mechanical separates of inorganic substances are given in Table I. The protein content as given was calculated from the nitrogen content, since it is known that practically all the nitrogen is present in the form of protein. A calculation by difference of protein was also made using the data of Tables I and II; the result checked closely with that based upon the nitrogen content.

TABLE I. GROSS COMPOSITION OF MILORGANITE

Constituents Determined	Air-Dry Basis %
Water (lost at 110° C.)	6.2
Protein	37.5
Cellulose	7.0
Fat	6.5
Fe <sub>2</sub> O <sub>3</sub> (free)	6.1
Sand	2.4
Silt	13.4
Clay	14.4
Total	93.5
	6.5 <sup>a</sup>

<sup>a</sup> Water not lost at 110° C., lignin, and various easily soluble salts.

Cellulose was determined by the crude-fiber method (1). Although pectin, some lignin, and related compounds, which are present in small amounts, are usually included under "crude fiber", they are here included under cellulose, being complex insoluble carbohydrates which have escaped biological digestion. The 7 per cent of cellulose present in milorganite is probably not sufficient to interfere with the availability of the nitrogen to plants because of temporary microbial fixation which is induced by excessive supplies of carbohydrates (8).

Fat, or ether-soluble extract, was determined by the usual standard procedure (1). Although an appreciable amount of fat—6.5 per cent—was found, because of its low activity it has no special significance as regards the fertilizer value of milorganite.

The mechanical separations of the inorganic materials were made essentially as described in a special case for soils (9). After leaching out fatty material with ether, the relatively

large amount of resistant organic matter remaining necessitated several treatments with 30 per cent peroxide to remove it. Two sodium sulfide-oxalic acid treatments with an intervening peroxide treatment were necessary to remove completely the free iron oxide and last traces of organic matter. The resulting light gray, silty residue, which resembled that obtained from an average soil by the same procedure, was mechanically separated into sand, silt, and clay fractions by sedimentation, using a centrifuge for the latter two fractions.

TABLE II. CHEMICAL COMPOSITION OF MILORGANITE

Constituents	Composite Sample, 1931-32			Water-free basis %	Composite Sample, 1931-37, Air-Dry Basis %
	1 %	2 %	Av. %		
H <sub>2</sub> O lost at 110° C.	7.240	7.260	7.250	.....	.....
Ignition loss with Mg(NO <sub>3</sub> ) <sub>2</sub>	63.620	63.540	63.580	68.550	.....
SiO <sub>2</sub>	7.800	7.880	7.840	8.452	.....
Fe <sub>2</sub> O <sub>3</sub>	6.630	6.630	6.630	7.148	.....
Al <sub>2</sub> O <sub>3</sub>	2.957	2.997	2.977	3.211	.....
CaO	1.541	1.567	1.554	1.675	.....
MgO	1.680	1.680	1.680	1.810	.....
K <sub>2</sub> O	0.795	0.804	0.800	0.862	0.807
Na <sub>2</sub> O	0.885	0.948	0.916	0.988	.....
TiO <sub>2</sub>	0.075	0.079	0.077	0.083	.....
MnO	0.0301	0.0304	0.0302	0.0327	0.025
CuO	0.0435	0.0427	0.0431	0.0465	0.0487
BaO	0.061	0.052	0.0565	0.0611	.....
ZnO	0.0145	0.0155	0.0150	0.01627	0.030
PbO	0.209	.....	0.209	0.225	.....
NiO	0.00526	0.00516	0.0052	0.00561	.....
CoO	0.00019	0.00018	0.000185	0.00020	.....
P <sub>2</sub> O <sub>5</sub>	2.880	2.850	2.865	3.089	3.180
SO <sub>3</sub>	2.640	2.740	2.690	2.900	2.93
Cl	0.463	0.467	0.465	0.501	.....
Cr <sub>2</sub> O <sub>3</sub>	0.203	.....	0.203	0.219	.....
As <sub>2</sub> O <sub>3</sub>	0.013	0.012	0.0125	0.01347	.....
B <sub>2</sub> O <sub>3</sub>	0.0038	0.0041	0.00395	0.00426	0.0115
Iodine	0.0010	0.0011	0.00105	0.00113	.....
Total			99.9131	99.9036	

The very low sand content indicates that the plant operation for removal of heavy coarse material such as sand is effective. The silt and clay fractions, as with soils, contained inorganic base-exchange material, and determinations by the usual method revealed exchange capacities of 26.2 and 31.1 milliequivalents per 100 grams, respectively. This is equivalent to an exchange capacity of 28.7 milliequivalents per 100 grams of the combined silt and clay as these occur in milorganite. The total exchange capacity of milorganite was found to be 22.4 milliequivalents per 100 grams, 5.9 milliequivalents of which are accounted for by the weighted capacity of the silt and clay, while the balance, 16.5 milliequivalents, is presumably due to organic matter. This rather high exchange capacity of milorganite may have some value as a reservoir for holding bases when large amounts of the material are applied to very sandy soils, which are generally lacking in this respect.

The free iron oxide was determined by analysis of the extract obtained in the sodium sulfide-oxalic acid treatment. This iron originates partly from the ferric chloride which is added for coagulation just prior to filtering. A small portion (see Table III) is present in the ferrous state, and represents iron which is very readily available for plant growth. Biological decomposition of the associated organic material undoubtedly results in the reduction and solution of more of the



iron oxide. Milorganite is thus probably a very good source of iron for plants, since plants absorb and utilize largely the ferrous form (4).

### Chemical Composition

A rather complete chemical analysis of the inorganic constituents of Milorganite is presented in Table III.

TABLE III. MAIN FERTILIZER CONSTITUENTS OF MILORGANITE

Constituents	Sample, 1931-32			Water-free basis	Composite Sample, 1931-37, Air-Dry Basis
	1	2	Av.		
	%	%	%	%	%
Nitrogen, total	6.060	6.040	6.050	6.52	6.04
Citrate-soluble $P_2O_5$	2.250	2.230	2.240	2.42	2.52
Citrate-insoluble $P_2O_5$	0.630	0.620	0.625	0.675	0.66
Water-soluble $P_2O_5$	0.0052	...	0.0052	0.0056	0.0041
Exchangeable $K_2O$	0.284	0.281	0.282	0.304	0.465
Exchangeable $Na_2O$	0.151	0.151	0.151	0.163	....
Organic and water-soluble $SO_3$	....	...	....	....	0.621
Water-soluble $B_2O_3$	....	...	....	....	0.0073
Ferrous iron	....	...	....	....	0.016
CuO, total	....	...	....	....	0.0431
Sol. in $CO_2$ -satd. $H_2O$	....	...	....	....	0.0035
Sol. in 0.002 $N H_2SO_4$	....	...	....	....	0.0461
MnO, total	....	...	....	....	0.0250
Sol. in $CO_2$ -satd. $H_2O$	....	...	....	....	0.0062
Sol. in 0.002 $N H_2SO_4$	....	...	....	....	0.0204
ZnO, total	....	...	....	....	0.030
Sol. in $CO_2$ -satd. $H_2O$	....	...	....	....	0.026
Sol. in 0.002 $N H_2SO_4$	....	...	....	....	0.032

After ashing, silica, sesquioxides, titania, the alkaline earth metals, and the alkali metals were determined by the usual methods. In the acid extract of the ash, cobalt and nickel were determined gravimetrically by precipitating with nitroso- $\beta$ -naphthol and dimethylglyoxime, respectively, and copper, manganese, and zinc colorimetrically as pyridine-thiocyanate complex, permanganate, and ferrocyanide, respectively. Chromium was determined iodometrically after fusion of the ash with sodium peroxide and solution in water. After ignition of a sample with excess magnesium nitrate and solution of the residue in acid, phosphorus was determined by titrations of the precipitated ammonium phosphomolybdate. Sulfur and chlorine were weighed as the respective barium and silver salts, which were precipitated from a solution of a sample after ignition with a mixture of magnesium oxide and sodium carbonate. Iodine was determined colorimetrically in the water extract of a sample after controlled ignition of the original material with potassium hydroxide. The Gutzeit method was used to determine arsenic. In the composite sample of Milorganite collected in the period 1931 to 1932, total boron was determined by titration after separation as the ester by distillation, while in the sample collected during the period 1931 to 1937 water-soluble boron was determined after extraction with boiling water by means of the quinizarin colorimetric method (3).

The data of Table II show that Milorganite contains appreciable amounts of many elements. Because of the diverse sources from which the material comes, one might expect the presence of at least traces of practically all the elements.

### Main Fertilizer Constituents

Results of analyses for essential plant nutrients by methods which reflect availability to plants are given in Table III. The copper, zinc, and manganese soluble in carbonated water and 0.002  $N$  sulfuric acid were determined by extracting 10 grams of 100-mesh Milorganite with 1000 cc. of the respective extractants and then applying the methods of determination mentioned above. The organic and water-soluble sulfur was determined by extraction with hot water after destruction of organic matter with bromine, and then precipitating and weighing as the sulfate. Exchangeable potassium was extracted by leaching with a neutral solution of ammonium acetate. Although nitrogen and phosphoric acid make up the chief portion of the available plant nutrients, the appreciable amounts of other nutrient elements including the minor ones given in the last column may well be of considerable im-

portance in certain cases. Based upon these figures, a ton of Milorganite contains the equivalent of 1.36 kg. of cupric sulfate pentahydrate, 0.95 kg. of zinc sulfate heptahydrate, 0.48 kg. of manganese sulfate tetrahydrate, and water-soluble boron equivalent to 0.18 kg. of borax. The high solubility of the minor nutrient elements in weak solvents indicates high degree of availability.

### Heteroauxin Production

Substances of the hormone type which are capable of promoting plant growth are classified in two groups—namely the auxins or natural plant hormones found in living plants and heteroauxin or indole acetic acid which is a product of animals and microorganisms. Thimann and Dolk (7) and Thimann (6) have shown that the latter type is produced when certain fungi are grown on media containing peptone and they have devised rather accurate methods of measuring small quantities. Since activated sludge is partly a microbial product, it seemed desirable to make tests for the presence of heteroauxin. Results were negative in every case.

Since the biological changes which nitrogenous organic matter undergo in the soil may be regarded as paralleling the growth of fungi upon media containing peptone, hormone production in the former case should be expected. Soil cultures, each containing 200 grams of sand, 100 grams of soil, and 50 grams of Milorganite were prepared, and after moistening were incubated in open Erlenmeyer flasks in the greenhouse. At intervals of 3 days, one of the cultures was examined for growth-promoting substances by extracting with 95 per cent alcohol, and purifying as recommended by Thimann (6). The product was then tested by the *Avena coleoptile* method described by Avery *et al.* (2), which is sensitive to a few tenths of a gamma of heteroauxin.

TABLE IV. HETEROAUXIN PRESENT AFTER 10 DAYS IN CULTURES OF MILORGANITE AND OTHER NITROGENOUS MATERIALS (Cultures: 50 grams of organics, 100 grams of soil, and 200 grams of sand)

Nitrogenous Substance	Percentage Nitrogen	Heteroauxin, Gammas per Culture
Milorganite	6.04	1.7
Cottonseed meal	6.54	2.4
Castor pomace	6.20	1.3
Fish scrap	9.56	4.0
Slaughterhouse waste	2.31	0.64
Ammonium sulfate (17.2 grams)	21.1	None
Urea (8.7 grams)	46.0	None

Results of these tests showed that measurable quantities of heteroauxin were present in the cultures after a few days of incubation, and that a maximum amount was present after 10 to 14 days of incubation. A continuous decline took place thereafter. Since control cultures gave negative results, it was evident that the hormone production was dependent upon the Milorganite added. Other common organics were then cultured in a similar manner, and hormone production after 10 days was found to be approximately proportional to the nitrogen contents of the organics added. These results together with the negative results obtained with two major protein sources of nitrogen—ammonium sulfate and urea—are presented in Table IV.

### Summary

Activated sludge, "Milorganite", consists approximately of the following substances: protein 37.5 per cent, cellulose 7.0 per cent, fat 6.5 per cent, free iron oxide 6.1 per cent, silica 2.4 per cent, silt 13.4 per cent, clay 14.4 per cent, and water 6.2 per cent. The balance of 6.5 per cent consists of phosphates, sulfates, and compounds containing calcium, magnesium, potassium, aluminum, titanium, sodium, and measurable amounts of manganese, copper, zinc, cobalt, boron, iodine, and many other elements. The appreciable quantities



es of the minor nutrient elements present, being easily soluble for the most part, may have significant fertilizer value in certain cases. The main fertilizer value is accounted for by the nitrogen and available phosphoric acid which are present to the extent of approximately 6 and 2.5 per cent, respectively. The material has a base-exchange capacity of 2.4 milliequivalents, a property which may be of some value when the material is applied to very sandy soils.

Tests made on the material directly failed to reveal the presence of plant hormones. However, after mixing and incubation of the material with a sandy soil, hormones of the dole-substituted fatty acid type were produced in amounts comparable to those produced with similarly treated fish meal, cottonseed meal, castor pomace, and tankage. Urea and ammonium sulfate failed to promote hormone production when mixed with the sandy soil.

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# Laboratory Columns for Close Fractionation

## Conical Type of Stedman Packing

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THE conical type of Stedman packing was developed by D. F. Stedman in the laboratories of the National Research Council of Canada at Ottawa and patented in the United States (15), Canada (12), and elsewhere. Stedman has reported the efficiencies obtainable with conical-type packing 2.5 cm. (1 inch) in diameter as determined by testing with mixtures of *n*-hexane and cyclohexane (10, 11, 13, 14). This packing is being further developed, and three sizes of the conical type have been produced, the operating characteristics of which are presented below.

### Description of Packing

The conical type of packing is made of wire cloth which has been embossed and trimmed into flat, truncated, conical disks. A semicircular hole is cut out of one side of the cone and extends about two thirds of the distance from the edge of the cone to the point in the center. The disks are welded together alternately back and edge to edge, so as to form a regular series of cells, with the holes which serve as vapor passageways located alternately on opposite sides of the section of packing. The construction may be readily understood by reference to Figure 1. The three sizes of packing on which tests are reported herein had nominal diameters of 25 mm. (0.984 inch), 19.0 mm. (0.750 inch), and 9.5 mm. (0.375 inch) and were called Nos. 112, 104, and 105, respectively.

The packing is customarily fabricated from stainless-steel wire cloth of  $15.75 \times 23.6$  meshes per cm. ( $40 \times 60$  meshes per inch), using wire 0.0229 cm. (0.009 inch) in diameter. It may, however, be made of any other material that can be drawn into wires and woven into wire cloth of the proper mesh, in accordance with the particular use to which the packing is to be put. Other mesh sizes will be satisfactory, so long as the packing has sufficient mechanical strength and the surface tension of the liquid is great enough to seal the openings of the mesh and prevent the passage of vapor through the mesh, but certain sizes of mesh and wire diameter are best (11).

In operation the liquid flows along the screen and seals the openings of the mesh. The liquid flows out toward the walls of the column on a cone that is concave downward, and then back toward the center of the column on a cone that is concave upward, which is welded to the first cone at the outer edge. The lower cone is welded to another still lower cone at the center and the liquid flows through the mesh at the point of junction, then outward toward the walls on this lower cone, and so on until the liquid drops off the lowest cone of the column. The vapor enters the space between two cones which are welded around the outer

edges, through the vapor hole in the lowest cone. It then flows through the space between these two cones, practically at right angles to the axis of the column, and out through the vapor opening in the upper cone of the pair. The vapor then divides and flows around the point where two cones are joined back to back, and across to the side of the column where it first entered the packing. This flow is then repeated until the vapor leaves the packing at the top of the column.

There is a continual mixing and separation of liquid and vapor, so that channeling is not possible. The tubing in which the packing is inserted must fit the packing closely, so that any openings between the packing and the tubing are sealed by the liquid to prevent by-passing of the vapor. The underside of the liquid stream

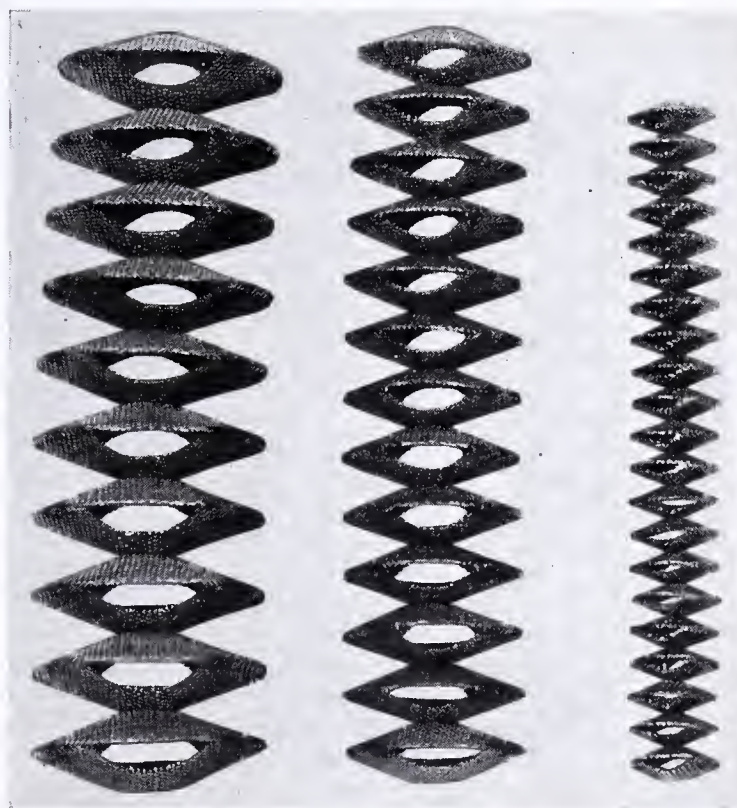


FIGURE 1. THREE SIZES OF STEDMAN PACKING, CONICAL TYPE



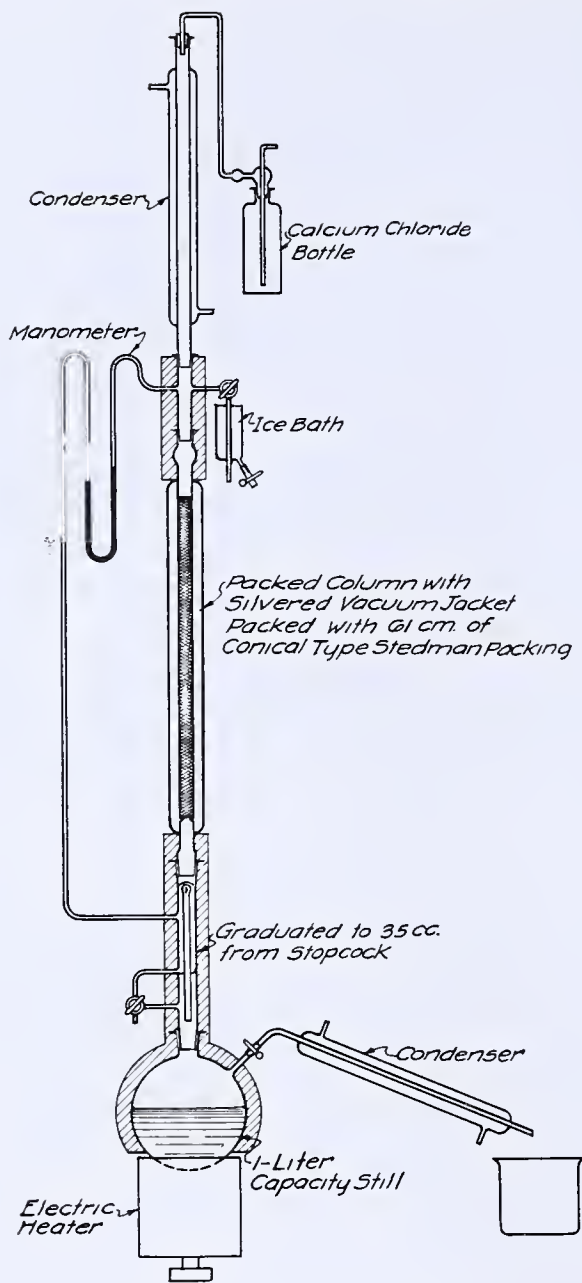


FIGURE 2. DIAGRAM OF COLUMN

is exposed to vapor as it flows along the mesh of the screen and the irregularities of the woven screen cause turbulence in the liquid stream, so that the liquid is well exposed to the vapors and the equivalent of an equilibrium contact is quickly attained.

Testing of Packing

The packings were tested in Pyrex glass columns equipped with silvered vacuum jackets and standard ground-glass joints, the inner tubes of which were carefully selected so as properly to fit the packings. The packings rested on three small indentations in the inner tubes and the height of the packed section was 61.0 cm. (24 inches) in all cases. The packed columns were connected to other apparatus as shown in Figure 2.

A binary mixture of benzene-ethylene dichloride was used in all tests. All tests were made at atmospheric pressure and with total reflux. The reflux rate was determined by turning the stopcock of the reflux collector below the column so as to interrupt the flow of reflux back to the still and noting the time required to collect a definite amount of reflux.

The reflux collector was also used to determine the drainable portion of the liquid holdup in the columns. At the end of a run the heat to the still was shut off, and at the same time the stopcock was turned to prevent return of reflux to the still and a pinch clamp was removed from the connection to

the auxiliary condenser. This allowed the vapors from the still to escape, so that they would no longer enter the column. The reflux that collected was the drainable portion of the holdup of the column. The nondrainable portion of the holdup was determined by pouring a measured quantity of the binary mixture through the previously dried columns, at room temperature and at a high rate, so that the packing was thoroughly wet, and measuring the quantity of liquid that

TABLE I. EFFICIENCY TESTS

Reflux Rate Cc./hr.	<sup>n</sup> <sub>D</sub>		Pressure Drop Mm. Hg (In. H <sub>2</sub> O) Cc.	Total Hold-up	Theoretical Plates in Column	H. E. T. P. Cm. (In.)
	Above packing	Below packing				
Packing 105, 9.5-Mm. (0.375-Inch) Diameter Empty Column						
100	1.4586	1.4509	.. ..	..	9.2	6.6 (2.6)
125	1.4586	1.4511	.. ..	..	8.8	6.9 (2.7)
150	1.4560	1.4512	.. ..	..	6.2	9.8 (3.9)
175	1.4555	1.4514	.. ..	..	5.3	11.5 (4.5)
200	1.4547	1.4515	.. ..	..	4.2	14.5 (5.7)
Packed Column						
90	1.4742	1.4512	0.09(0.05)	..	20.0	3.05(1.20)
100	1.4878	1.4497	0.09(0.05)	..	32.6	1.87(0.74)
110	1.4959	1.4506	0.18(0.10)	5.7	41.6	1.47(0.58)
130	1.4997	1.4519	1.5 (0.8)	7.7	53.6	1.14(0.45)
140	1.4996	1.4498	2.2 (1.2)	7.1	56.4	1.08(0.42)
150	1.4997	1.4502	4.1 (2.2)	7.9	56.4	1.08(0.42)
170	1.4994	1.4507	4.5 (2.4)	8.0	53.3	1.14(0.45)
170	1.4997	1.4528	5.1 (2.75)	..	52.2	1.17(0.46)
180	1.4963	1.4476	6.5 (3.5)	8.5	49.9	1.22(0.48)
190	1.4986	1.4536	7.5 (4.0)	8.7	44.8	1.36(0.54)
200	1.4955	1.4489	7.9 (4.2)	8.7	44.2	1.38(0.54)
210	1.4968	1.4519	9.1 (4.9)	8.7	41.5	1.47(0.58)
212	1.4965	1.4518	9.3 (5.0)	8.3	40.9	1.49(0.58)
225	1.4972	1.4544	12.1 (6.5)	8.9	39.1	1.56(0.61)
262	1.4979	1.4540	13.7 (7.35)	..	41.7	1.46(0.58)
230	....	....	13.1 (7.0)	Flood point		
Packing 104, 19.0-Mm. (0.750-Inch) Diameter Empty Column						
150	1.4593	1.4514	.. ..	..	9.0	6.8 (2.7)
200	1.4564	1.4513	.. ..	..	6.4	9.5 (3.8)
250	1.4543	1.4511	.. ..	..	4.3	14.2 (5.6)
250	1.4528	1.4500	.. ..	..	4.4	13.8 (5.5)
450	1.4522	1.4514	.. ..	..	1.2	50.8(20.0)
500	1.4520	1.4512	.. ..	..	1.3	46.9(18.5)
700	1.4523	1.4515	.. ..	..	1.2	50.8(20.0)
900	1.4522	1.4515	.. ..	..	1.0	61.0(24.0)
Packed Column						
100	1.4970	1.4511	0.15(0.08)	8.7	43.2	1.41(0.55)
125	1.4984	1.4509	0.37(0.20)	10.7	48.0	1.27(0.5)
150	1.4989	1.4508	0.47(0.25)	10.7	50.3	1.21(0.4)
175	1.4980	1.4493	0.7 (0.4)	10.7	49.5	1.23(0.4)
200	1.4982	1.4503	1.2 (0.65)	17.2	48.3	1.26(0.5)
300	1.4941	1.4486	2.3 (1.25)	18.0	42.7	1.43(0.5)
400	1.4926	1.4502	8.4 (4.5)	20.7	36.7	1.66(0.6)
500	1.4898	1.4501	11.6 (6.2)	21.2	33.7	1.81(0.7)
600	1.4908	1.4526	13.8 (7.4)	24.7	30.6	1.93(0.7)
637	1.4883	1.4529	16.8 (9.0)	..	27.8	2.19(0.8)
637	....	....	16.8 (9.0)	Flood point		
Packing 112, 25.0-Mm. (0.984-Inch) Diameter Empty Column						
150	1.4639	1.4514	.. ..	..	12.5	4.8 (1.8)
200	1.4586	1.4508	.. ..	..	10.3	5.9 (2.3)
350	1.4528	1.4510	.. ..	..	2.7	22.6 (8.9)
500	1.4520	1.4510	.. ..	..	1.7	35.8(14.1)
700	1.4526	1.4514	.. ..	..	1.7	35.8(14.1)
800	1.4524	1.4513	.. ..	..	1.6	38.1(15.0)
900	1.4522	1.4511	.. ..	..	1.6	38.1(15.0)
Packed Column						
128	1.4908	1.4484	0.15(0.08)	8.4	38.7	1.62(0.6)
150	1.4979	1.4497	0.18(0.10)	9.0	48.4	1.25(0.5)
160	1.4970	1.4488	0.18(0.10)	..	48.0	1.27(0.5)
200	1.4975	1.4516	0.37(0.20)	13.0	43.8	1.39(0.5)
250	1.4922	1.4482	0.65(0.35)	14.5	41.0	1.49(0.6)
280	1.4902	1.4482	0.84(0.45)	17.0	38.7	1.57(0.6)
300	1.4900	1.4482	1.03(0.55)	..	38.5	1.58(0.6)
400	1.4929	1.4516	1.7 (0.90)	22.4	34.8	1.75(0.7)
480	1.4889	1.4500	2.2 (1.2)	..	33.0	1.85(0.7)
500	1.4845	1.4464	3.0 (1.6)	24.0	31.1	1.96(0.7)
600	1.4798	1.4479	4.7 (2.5)	..	31.1	1.96(0.7)
700	1.4802	1.4485	6.3 (3.4)	27.0	29.5	2.06(0.8)
800	1.4813	1.4494	9.0 (4.8)	..	28.2	2.16(0.8)
900	1.4826	1.4508	12.1 (6.5)	33.0	26.3	2.32(0.9)
1000	1.4816	1.4514	15.9 (8.5)	34.0	24.6	2.48(0.9)
1080	1.4812	1.4514	17.7 (9.5)	35.8	24.2	2.52(0.9)
1125	1.4774	1.4493	20.6(11.0)	83.0	25.5	2.49(0.9)
1080	....	....	17.7 (9.5)	Flood point		



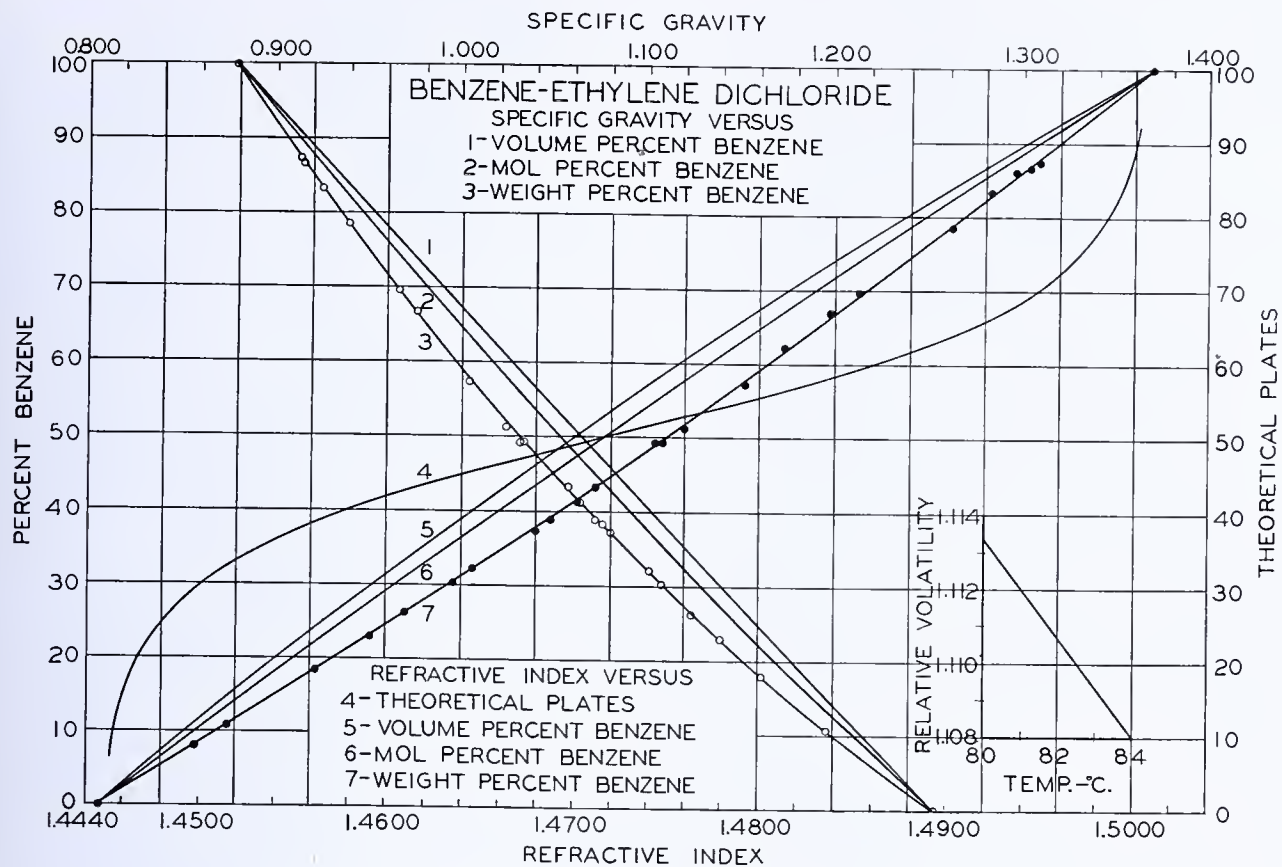


FIGURE 3. PLOT FOR DETERMINATION OF THEORETICAL PLATES

ld drain from the packing. This portion of the holdup was found to be 0.7, 2.7, and 3.0 cc., respectively, for the packings 105, 104, and 112 in the 61.0-cm. packed columns. The nondrainable reflux quantity determined in this manner will be slightly high, as it was determined with cold liquids.

The flood points were determined by increasing the distillation rates by substantially equal steps and noting the point at which the bottom reflux rate decreased suddenly. The packing was also observed closely and it was found that the point of sudden change in the reflux rate was the point at which a definite flooded condition was observed between some pair of cones. This point of initial flooding was generally near, but slightly above, the lower end of the packing.

Shortly after the testing was commenced, it was found that it was necessary to wet the packing thoroughly before the full efficiency could be developed. Otherwise, channeling of the liquid seemed to occur at the top of the column. This fact has been previously reported by Nickels (8) and Fenske, Lawroski, and Tongberg (4). The packing was wet by running the column at a rate above its capacity until it became completely flooded. The rate of distillation was next reduced until the flood subsided and then set at the point desired for the test being run.

The efficiency varied considerably with the rate of distillation, being better the lower the rate, until a peak was reached at a point after which the efficiency decreased rapidly with further reduction in the rate. It is believed that the peak represents the lowest rate at which it is possible, under continued

operation, to keep the screens thoroughly wet. Fleming (6) also noted that the efficiency was highest at very low rates of distillation.

It also soon became evident that comparatively long periods of uninterrupted operation were necessary to develop the full efficiency. By taking samples on fixed time schedules,

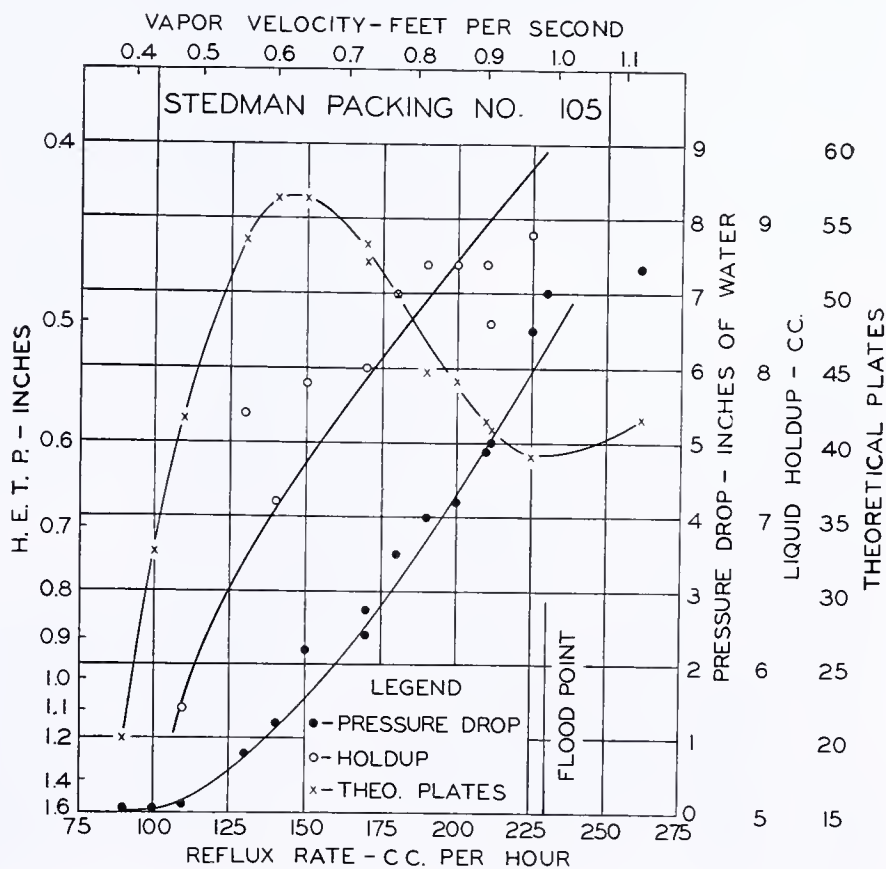


FIGURE 4. CHARACTERISTICS OF 9.5-MM. (0.375-INCH) DIAMETER PACKING



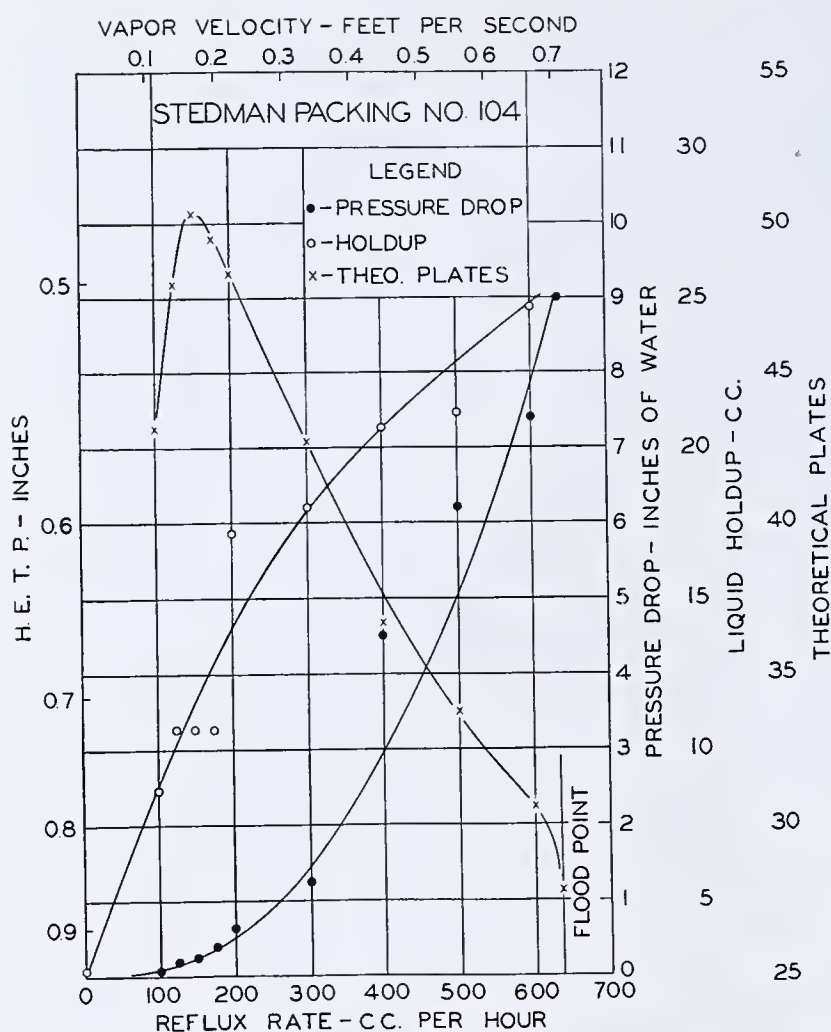


FIGURE 5. CHARACTERISTICS OF 19.0-MM. (0.75-INCH) DIAMETER PACKING

such as every hour, it was possible to set up a condition of false equilibrium in which the upset caused by removal of the sample was just offset by the continuation of the test to the period for taking the next sample. At low rates of distillation, particularly with the smallest packing, it was found advisable to continue the distillation for 5 hours before taking the first sample and then to take samples only every 3 hours. In all cases the distillation was continued until successive samples showed check results or at least a substantial check.

### Analysis of Samples

The reflux samples removed from above and below the packing were analyzed by refractive index and the number of theoretical plates was calculated by means of the equation of Beatty and Calingaert (1) which is a slight modification of that of Underwood (17), using values of relative volatility reported by Smith and Matheson (9). The values of relative volatility are nearly constant over the atmospheric pressure boiling range of mixtures of benzene and ethylene dichloride, but the slight error attendant upon the use of an average value of relative volatility was avoided by using a plot of theoretical plates *vs.* refractive index. This plot was constructed from calculations based on the equation of Beatty and Calingaert, using the corresponding values of relative volatility, so that readings could be made for the refractive indices of the samples removed from above and below the packing and the number of theoretical plates in the column could be determined as the difference of the two readings.

The method used for determining the efficiency of the columns loses its accuracy when the mixtures become too

dilute with respect to either constituent. Consequently, the liquid in the still was maintained at a benzene concentration of about 10 mole per cent.

The data used for the specific gravity and refractive index of various mixtures of benzene and ethylene dichloride were determined in the Foster Wheeler Corporation laboratory. The refractive index of purified benzene was found to be 1.5008 at 20° C. and that of purified ethylene dichloride to be 1.4441 at the same temperature. The data and plot used are shown as Figure 3. Both the benzene and the ethylene dichloride, as used, were obtained by distillation of a heart cut from purified benzene and ethylene dichloride. The two liquids were distilled with high reflux ratios and the distillates were sampled frequently. Only heart cuts having constant refractive index were saved for use in the binary mixtures.

Over the range of 15° to 30° C., the correction factor for the refractive index of benzene is  $-0.0006$  and for ethylene dichloride is  $-0.00053$  per °C. Using these factors to correct the refractive indices at 25.2° C. reported by Brunn and Schickanz (3) to 20° C., the author obtained 1.5007 and 1.4446, respectively, for benzene and ethylene dichloride; and similarly correcting the data of Hall and Bachman (7) he obtained 1.5008 and 1.4450, respectively.

### Test Results

The test results obtained on the three sizes of packing, as well as results obtained with the empty columns, are shown in Table I and are presented graphically in Figures 4 to 6.

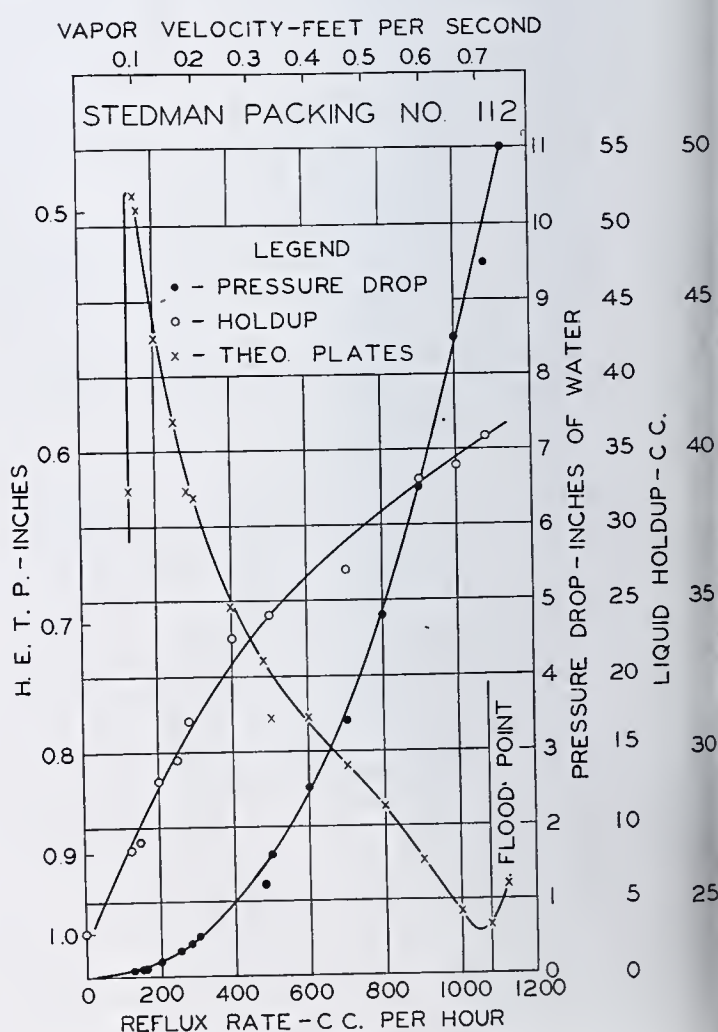


FIGURE 6. CHARACTERISTICS OF 25-MM. DIAMETER PACKING



In a few cases the liquid holdup values are not reported, because it was desirable at times to continue the operation of the column after equilibrium had been attained and by changing the distillation rate to make a new test run. It was found that the same equilibrium efficiencies could be determined in this manner in a much shorter time without reflooding the column as those obtained by starting with a freshly flooded column. This was particularly true when the second run was at a higher rate than the first, so that the second equilibrium efficiency was lower than the first. In such cases the holdup values could not be determined.

There have been no direct comparisons made in this laboratory, using the same technique and test methods, but assuming that the results obtained in this laboratory are comparable with those obtained by others (2, 4, 5, 7, 16), it will be evident that at comparable vapor velocities better efficiencies are possible with Stedman packing than with other types of packing. These efficiencies are accompanied by unusually low liquid holdup and by pressure drops that compare favorably with those of other types of packing. The throughput is also satisfactory and compares well with other packings as indicated by the possible superficial vapor velocities of 21.6 to 29.8 cm. (0.71 to 0.98 feet) per second for the three sizes of packing.

With these conical-type Stedman packings it will be possible to build columns having as many as 200 theoretical plates for use in the average laboratory. Such columns could open up new fields of possible close fractionations and analysis by means of distillation.

## Acknowledgment

The author wishes to acknowledge the services of L. Nilssen and S. Finelli, who conducted most of the laboratory tests, and of D. D. Davis, who worked up many of the data.

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# Antifoaming Devices

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GASTROCK and Reid (2) have recently described an antifoaming device and mentioned the essential feature of all methods which are suited to prevent carry-over of priming liquids: the rupture of the foam bubbles on top of the liquid level. The mechanism of priming (foaming) will be discussed elsewhere (4). The experiments establishing this mechanism have led to the conclusion that priming depends on the rate at which the steam nuclei can unite into larger bubbles and thus on the viscosity of the liquid and the electrostatic charge of the gas or steam bubbles.

Gastrock and Reid's hot wire antifoaming device might be considered to require a comparatively high energy input. The wire must be kept continuously at a fairly constant temperature. In addition it is in danger of becoming coated by material which may dry and burn.

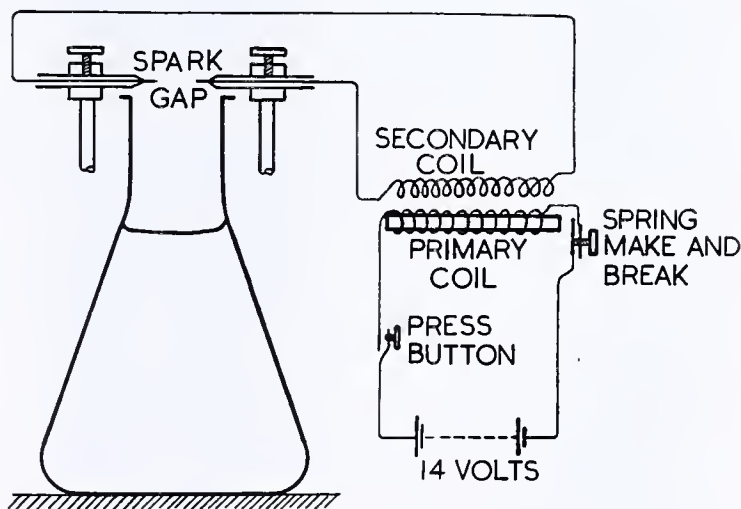


FIGURE 1. DIAGRAM OF EQUIPMENT

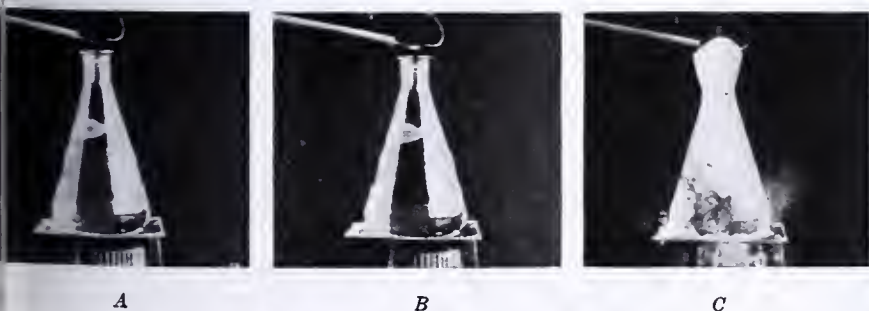


FIGURE 2. POSITION OF SPARK GAP

- A. Position of spark gap above neck of flask
- B. Spark
- C. Priming with heavy carry-over of liquid, as obtained without operating spark

Pictures A and B taken before liquid started to boil



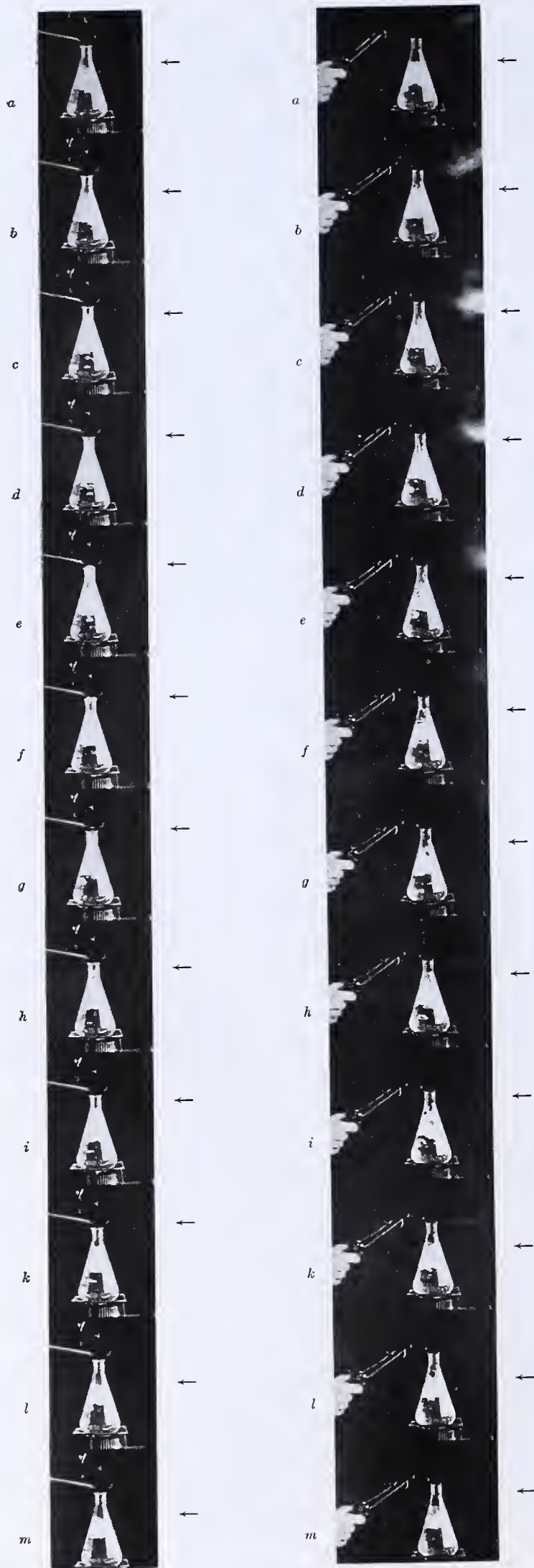


FIGURE 3 (Left). APPLICATION OF SPARK TO PREVENT CARRY OVER

a-d. Rise of liquid level  
e-m. Operation of spark and subsequent fall of level  
e-h. Spark kept on for about 0.25 second  
Foam level shown by arrows

FIGURE 4 (Right). USE OF WEAK AIR JET TO PREVENT CARRY OVER

Large foam bubbles are ruptured at stage represented by d and e. Subsequently the liquid level falls. Foam level shown by arrows

These disadvantages are not inherent in two alternative methods, both of which work on the principle of destroying the large bubbles on top of the liquid level, thus helping the remaining bubbles to join and break away from the surface. One of these methods applies an electric spark for breaking up the bubbles, the other a weak jet of air or any other gas. Both methods can be applied intermittently.

Figure 1 illustrates the equipment used. The liquid used in the examples shown in Figures 3 and 4 is a solution of soap in water.

Figure 2, A, shows a spark gap put a few millimeters above the mouth of a 500-cc. conical flask. In B, the spark, obtained from a small motor-car induction coil operated on 14 volts, can be seen traversing the gap. C illustrates a violent burst of priming with heavy carry-over while the spark is not operating. Application of the spark for less than 0.25 second ruptures the uppermost bubbles and causes the liquid level to fall, preventing carry-over of liquid. Figure 3 illustrates this.

The speed of the film was 16 pictures per second. a to c show the rise of the liquid (foam) level. At the stage represented by e the spark is initiated (a white horizontal streak at top of the foam level can be seen) and is kept on until the stage represented by h is reached. The liquid level continues to fall and to rise again later, as priming always takes place in short-lived bursts. This fact suggests the possibility of operating the spark automatically by means of a liquid level control—e. g., in a boiler or a distillation apparatus—instead of by the press button indicated in Figure 1.

The arrangement shown in Figure 1 is directly applicable to an analytical procedure. Application of the method in a boiler would require mounting the spark gap or the system of spark gaps at the entrance of the steam pipe.

The alternative method applies a weak jet of air or any other gas or steam across the mouth of the flask containing the priming liquid (Figure 4). The principle of the gas jet has been described by Friedrichs (1) and by Gerritz (2). Although the air jet was kept on continuously in the series demonstrated in Figure 4, it acted only when the large foam bubbles reached the mouth of the flask, d, e. a to c show the rise of the liquid level, f to m its falling.

This method can also be used for inflammable liquids and can be operated by means of a liquid level control. In applying this method care ought to be taken not to stir the liquid from the jet into the liquid, as a further supply of gas would promote priming.

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# Glass Helices for Packing Laboratory Fractionating Columns

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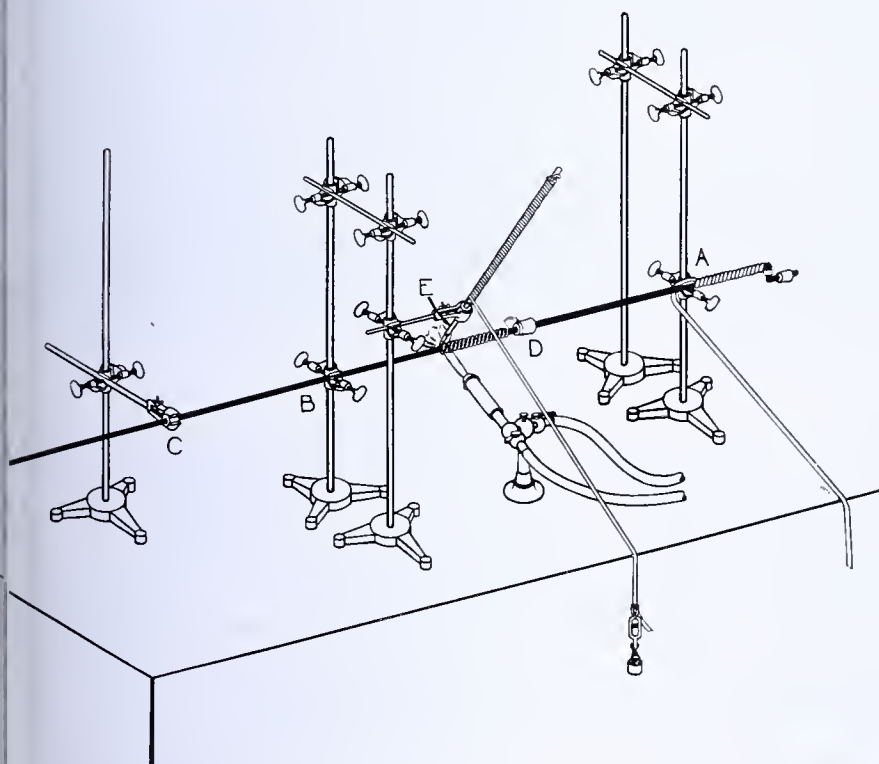


FIGURE 1. DIAGRAM OF APPARATUS

RECENTLY the need arose in this laboratory for a quantity of single-turn glass helices to be used as pack-  
for a fractionating column. A survey of the literature  
ed to reveal a suitable process intermediate between a few  
her arduous methods (1, 3, 4) requiring considerable adroit-  
s on the part of the operator, and the excellent but intricate  
mechanism of Stewart (2).

With very little practice the following method yields a  
form spiral which is easily withdrawn intact from the steel  
upon which it is wound, or broken into single-turn helices  
h negligible loss while still on the rod. Two operators are  
quired and all materials, with the possible exception of the  
el rod, are available in any chemistry laboratory.

## Description of Apparatus

The apparatus consists essentially of a suitably supported  
mandrel upon which is wound a spiral drawn from a 5-mm.  
Pyrex rod (Figure 1). In this instance the authors used a 120-  
cm (4-foot) length of 0.47-cm. (0.1875-inch) steel rod bent at  
one end to form a small crank. Two loosely turned up right-  
angle clamps, A and B, and cork C serve as bearings and prevent  
slipping of the mandrel as it is turned. Cork D, tightly fitting  
the rod, serves as an anchor for a small glass ring to which the  
drawing of each glass spiral is fused.

Uniform spacing of the spiral is accomplished by tying a  
length of pliable cord to the crank and allowing this to wind up  
the mandrel while turned by one operator. The front of the  
drawn spiral thus formed runs against the side of clamp A and  
causes a displacement of the mandrel equal to the diameter of  
the cord for every revolution. The unused cord is conveniently  
draped over the top of clamp A and a slight tension maintained  
allowing it to run through the thumb and index finger of the  
other hand. A loosely fitting cork handle on the crank facilitates  
both turning of the mandrel. Spirals of widely varying pitches  
can be produced by using cords of different diameters.

To draw a spiral of uniform fiber diameter  
it is essential that the glass rod be advanced  
at a constant rate. This is accomplished as  
follows:

A convenient length of Pyrex rod is closely  
wound from one end to a suitable length from  
the other with a length of soft cord. Sufficient  
glass is allowed to remain uncovered to extend  
from the top of the metal guide, E (a cork borer  
of the proper diameter mounted in a cork), to  
the steel mandrel. The free end of the cord is  
draped over the edge of the desk and held taut  
by means of a small weight appropriately fastened  
with a battery clamp. A slight downward pres-  
sure while slowly and evenly unwinding the cord  
from the glass rod causes it to advance at a uni-  
form rate.

## Procedure

The tip of the Pyrex rod is fused to the glass  
ring on the anchor and using an air-blast flame  
about 7.5 cm. (3 inches) long the mandrel is  
slowly turned to start the spiral. After a few  
turns the rate is increased to about 90 r. p. m.  
which is maintained to the end. As glass is  
drawn from the Pyrex rod it is slowly and

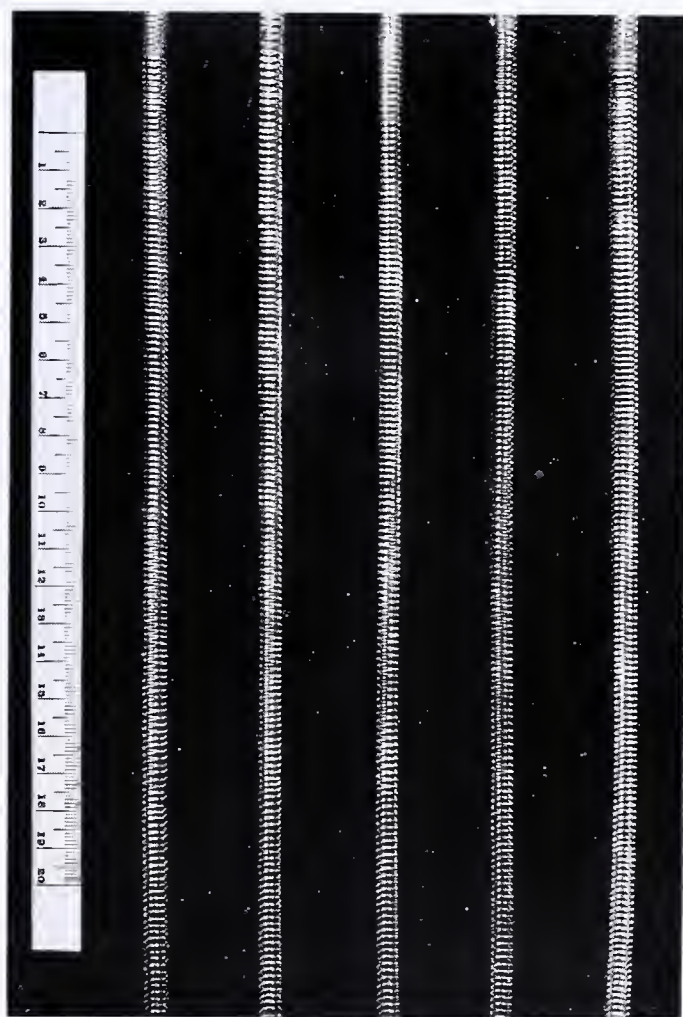


FIGURE 2. TYPICAL SPIRALS



uniformly advanced by a second operator. The blast flame is so adjusted that the outer brush is tangent to the mandrel and the tip of the inner cone just touches the glass rod.

When a spiral has been drawn the Pyrex rod is quickly withdrawn to part the glass. The mandrel is removed by unscrewing clamps *A* and *B*, and the spiral is broken away from the ring and slipped off. After replacing the mandrel and rod another spiral can immediately be drawn.

One critical adjustment is necessary in the position of the Pyrex rod. The elevation from the horizontal makes little difference, but it is essential that the longitudinal axis of the rod intersect the axis of the mandrel and be about perpendicular to it.

Using this method a uniform spiral 35 cm. long can be drawn, removed from the mandrel, and the apparatus reassembled ready for another spiral in about 4 minutes.

Several suggestions have been made for breaking spirals into individual single-turn helices (1, 2, 4). The authors found that negligible waste resulted if the spiral were returned to the mandrel, and individual helices broken apart by twist-

ing the blade of a spatula or other similar blunt instrument between individual turns. Nonuniform spirals are difficult to remove from the winding form and yield considerable waste upon being broken into helices.

In a typical operation 15 cc. of single-turn helices were obtained in 20 minutes from four 28-cm. spirals weighing 2.8 grams. Waste material amounted to 0.1 gram or about 3 per cent by weight. Spirals have averaged 5.9 mm. in outside diameter with an individual fiber diameter of 0.6 mm. A few typical examples are shown in Figure 2.

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# Semiautomatic, Multiple, Electrometric Titration Apparatus

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An apparatus is described in which ten electrometric titrations can be performed simultaneously by one operator within nearly as short a period as is required for a single titration. The burets are controlled by solenoids and the progress of the titration is followed by a series of colored lights on a control panel. While the apparatus was designed primarily for use in a fish-freshness titration, it can be used for a wide variety of potentiometric titrations.

When applied to the determination of the freshness of fish, the apparatus enables a single operator to conduct freshness tests on a mass scale which would require six to eight operators using the ordinary single-titration method. A practical application foreseen by the authors is the predetermination of the freshness of all fish landed on the Boston Fish Pier to enable sale price to be based upon quality.

THE electrometric method for determining the freshness of fish, as proposed by Stansby and Lemon (5), was studied further by Fitzgerald and Conway (1) to determine the practicability of its use in the commercial grading of fish. These studies showed an excellent correlation between freshness as indicated by electrometric titration and organoleptic tests conducted by expert fish buyers of long experience in judging the quality of fish. It was apparent, however, that if the method was to be applied in industry, certain

modifications would be required to permit the handling of a considerable number of samples simultaneously. In commercial practice, data on a large number of samples taken from different fishing vessels, and from different sections of the hold of each vessel, must be available within a relatively short period. Accordingly, a multiple-unit apparatus has been constructed which allows an operator to handle up to 10 samples at a time. The apparatus is suitable for making a wide variety of potentiometric titrations and hence is described here in some detail.

### Description of Apparatus

The circuit consists essentially of 10 sample titration half-cells connected individually, one after the other, by means of an automatic switching arrangement through a galvanometer to a reference electrode. The principle employed is that of Treadwell and Weiss (6), whereby the reference half-cells contain a solution having a pH identical with the desired titration end point, at which the galvanometer deflection will be zero. The automatic switch connects the titration cells into the circuit successively at 3-second intervals. Thus a galvanometer reading is obtained for each particular sample once every 30 seconds, and the progress of the titration is followed accordingly. The presence of any one cell in the circuit is indicated by one of 10 flashing amber lights on the control panel.

The titration burets are manipulated from the control panel and the flow of acid is controlled by solenoid cut-offs. When an end point for any cell is reached, as indicated by a zero deflection of the galvanometer at the instant the cell is cut into the circuit, the operator can throw a switch which cuts off the corresponding buret. At the same time a warning red light turns on, indicating that the particular buret has been turned off. A general view of the entire apparatus is given in Figure 1.



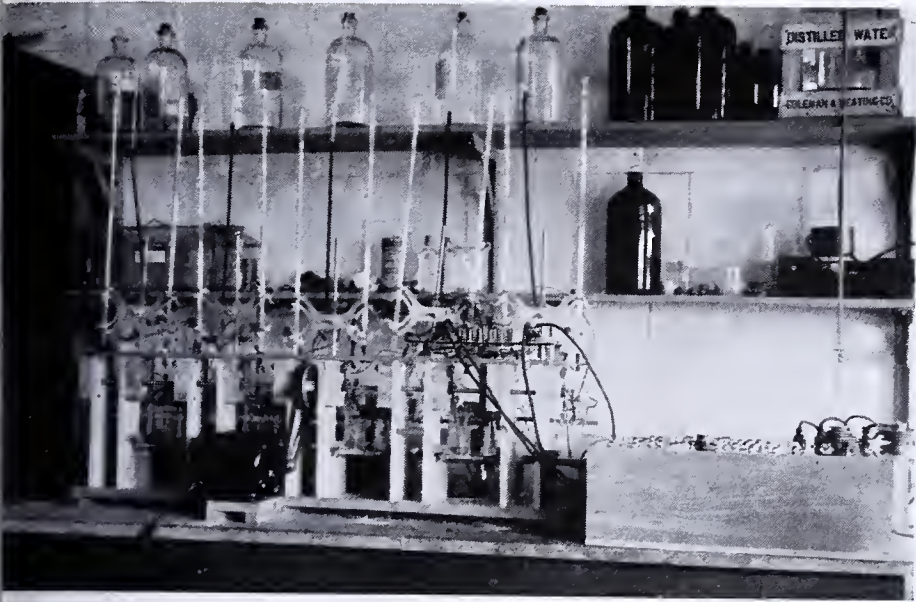


FIGURE 1. GENERAL VIEW OF TITRATION APPARATUS

The control panel is shown in Figure 2. The main galvanometer, A, at left center of the panel, is located centrally, with respect to the various lights and switches involved during the course of the titration.

The 10 toggle switches, G, control the solenoid buret cutoffs, and also operate the red warning lights, F, indicative of completed titrations. The flashing amber lights are shown as E. The green lights, D, are controlled by toggle switches C. When any of these switches are in the off position (adjacent green lights off) the corresponding titration cells are completely disconnected from the circuit, regardless of the position of the automatic switch.

The apparatus is designed to permit alternate use of 2 reference electrodes. Connection to either electrode is made through toggle switch J, and amber light L or green light M indicates which is in the circuit. Toggle switch H connects the alternating current power to the control panel, and also turns off the power to the solenoid buret cutoffs. Thus, all burets can be operated simultaneously by switch H, individually by the proper switch, G.

Toggle switch K, designated as the master switch, disconnects all cells from the galvanometer circuit. This is provided to reduce the total resistance of a cell in the circuit during a titration, thus minimizing polarization. The off position is indicated by red light P, and the on position by amber light N.

The control panel is equipped also with an auxiliary, manually operated, rotary, 10-point switch, U, and an auxiliary galvanometer, B. By depressing push button T, the main galvanometer is disconnected and replaced in the circuit by the auxiliary galvanometer. In this case, the titration to be connected to the galvanometer can be selected manually by the auxiliary rotary switch. Both galvanometers are at Leeds & Northrup, No. 24-D, without mounting cases.

The automatic selector switch is mounted beneath the panel at W. Cable connections from the solenoid-

operated burets, and from the electrodes, enter the panel circuit through the 4 radio tube sockets, X.

The automatic selector switch, shown at the extreme right of Figure 3, consists of a 2-gang, rotary, 10-point switch. One gang makes contact with each point for  $\frac{1}{10}$  of the rotational period, and is used for connecting the amber lights, E, into the alternating current circuit. The other gang connects the titrations into the galvanometer circuit. In this case, however, only momentary contact is made, so as to connect the electrodes to the galvanometer for just sufficient time to give a satisfactory deflection. This adjustment is somewhat critical, since continued contact increases polarization of the electrodes, while insufficient contact reduces the sensitivity of the galvanometer, and the best adjustment must be determined on the basis of experience. The switch is rotated by belt drive to a set of cone pulleys on shaft W, from a Merkel-Korff motor and gear-reduction unit No. S-615, which is mounted on one outside edge of the panel case.

The 110-volt, alternating current power for the apparatus is distributed to the rotary switch motor, the control panel alternating current circuit, and titration assembly by means of two double electric outlet sockets, connected in parallel, one being mounted on each end of the panel case. By using this system a flexible arrangement is attained, so that by removing the plugs from the sockets and the pulley belts, the Bakelite panel can be removed.

The titration assembly, shown in Figure 1, consists of 10 solenoid-operated burets, a battery of 10 stirring units with supports for 10 sample cells, the electrode system, a potassium chloride connecting system including agar bridges and potassium chloride trough, and a Bakelite connection panel.

The solenoid burets are constructed somewhat like those described by Shenk and Fenwick (3), but differ in the following respects: In the original Shenk and Fenwick burets the flow of reagent is stopped by turning off the solenoid, whereas in the present case the clamp is designed to turn on the flow of reagent

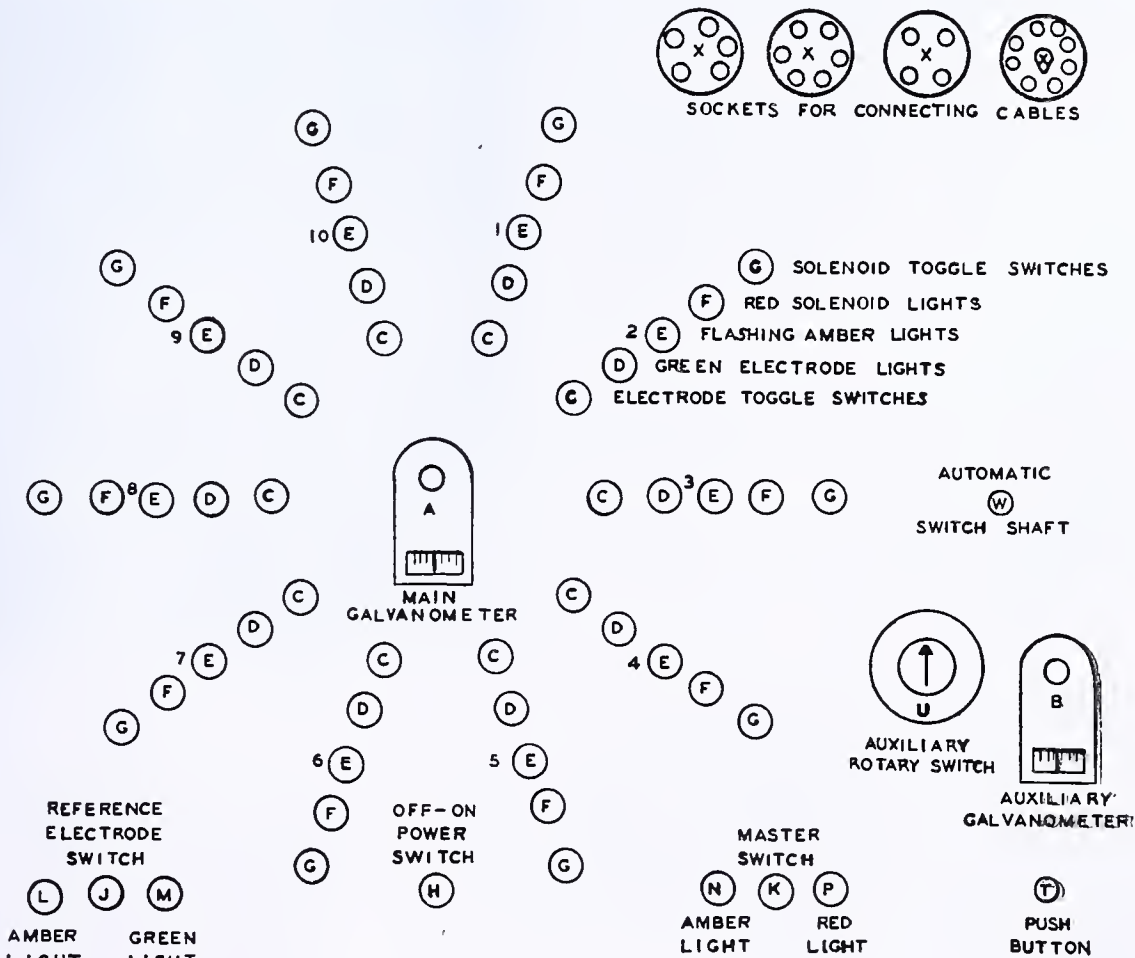


FIGURE 2. DIAGRAM OF CONTROL PANEL



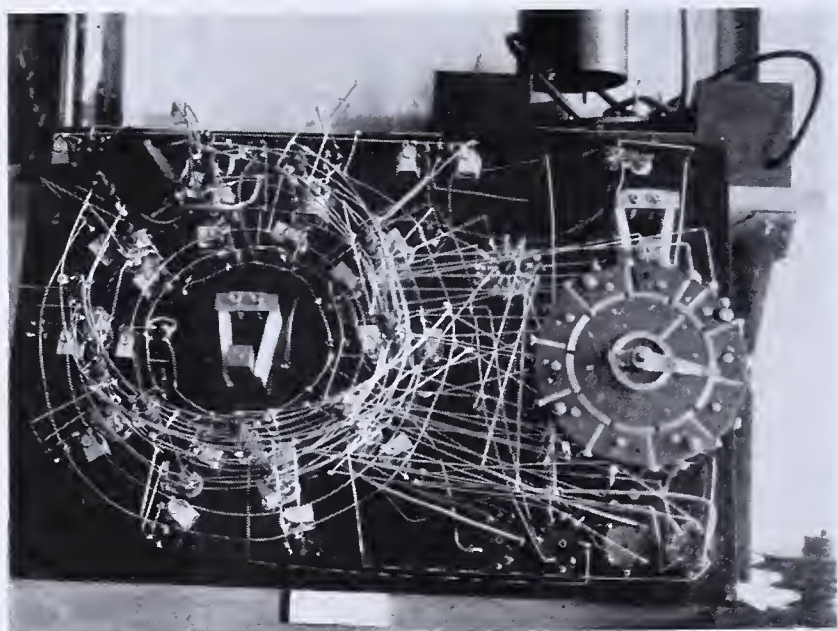


FIGURE 3. WIRING OF CONTROL PANEL

when the solenoid is turned off. Also the tension in the spring is adjusted so that it is not necessary to reset the clamp manually in order to start the flow of reagent.

The battery of 10 electrically driven stirrers is mounted on a wooden platform 130 cm. long. The stirrers consist of Monel metal rods with spiral shaped paddles made from Monel metal wire and are fastened by Bakelite insulating couplings to rods which are rotated by being geared to a horizontal countershaft, driven by a 0.125-horsepower electric motor. The beakers used for the sample cells are supported beneath the stirrers on wooden shelves which in turn are supported by a rod and thumb catch. By releasing the thumb catch, the shelf pivots about the rod so as to lower the beaker from the rigid stirrer. Figure 4 shows a close-up view of stirrer, beaker, and solenoid cutoff.

Quinhydrone electrodes for both the sample and reference cells consist of 1 sq. cm. of platinum foil attached to 10-cm. lengths of platinum wire. The reference half-cells are contained in small vials fastened to a small wooden platform. The electrodes in the sample cells are held in place by means of the support, described by Stansby (4). The agar bridges from the 10 sample and 2 reference half-cells dip into a long wooden trough, containing saturated potassium chloride solution, extending the length of the apparatus.

Connections from the electrodes and solenoids to the control panel are made at a Bakelite connection panel. This panel which is 35 cm. long and 12.5 cm. wide, contains small radio-type plug jacks for the solenoids, and radio tube sockets for the electrode connections. Four different types of radio sockets are used, in order to eliminate any possibility of making a wrong connection. The connection panel can be seen in Figures 1 and 4. Contact between the control panel and connection panel is made by means of cables, having corresponding plugs at each end.

### Operation

The apparatus is capable of considerable flexibility in manipulation, and since many different problems may be expected in the field of electrometric titrations no one schedule of operations can be recommended as most suitable for every problem. Even in the fish titrations, it was found from experience that certain situations required modifications in the continuity of operating procedure. The following procedure, therefore, may be considered as meeting the average situation when determining simultaneously the freshness of a number of samples of fish.

The burets are filled with the titration reagent and are held shut by pinchclamps. This is necessary because, as described previously, the solenoid-operated buret clamps are open when the current is off, and closed when the solenoid is energized.

The 10, or fewer, samples are placed in position on the sample cell supports, and the electrodes and agar bridges are attached. If the operator is beginning a day's testing, the reference electrodes are also filled with fresh buffer solutions of the desired end points of the titrations.

When the samples are in position and the above mentioned connections have been made, the alternating current power is turned on by means of switch *H*. If not already so, the master switch, *K*, is turned to the off position and is kept in this position during the titrations, except when actual galvanometer observation are being made, in order to minimize polarization of the electrodes. The solenoid toggle switches, *G*, are then turned to the on position (all the red lights, *F*, on). The electrode toggle switches, *C*, are also turned to the on position, this being indicated by the green lights, *L*. If less than 10 samples are being tested, the green lights corresponding to electrodes not in use should be turned off. The apparatus may now be considered in readiness for beginning the titration.

The automatic switch motor is turned on and the master switch opened while the violence of the galvanometer deflection for each of the samples is observed. In the fish titration and others involving systems fairly well buffered at the end point, the violence of the galvanometer deflection is roughly indicative of the proximity of the end point. After some experience with the particular system, the operator will be able to estimate from the galvanometer deflection the approximate amount of reagent required to reach the end point in each titration. The pinchclamps on the burets are then released and the flow of acid is started by turning off the alternating current power switch.

The quantity of reagent added to each cell should be slightly less than that estimated as necessary to bring the cell giving the weakest initial galvanometer deflection to the end point. The

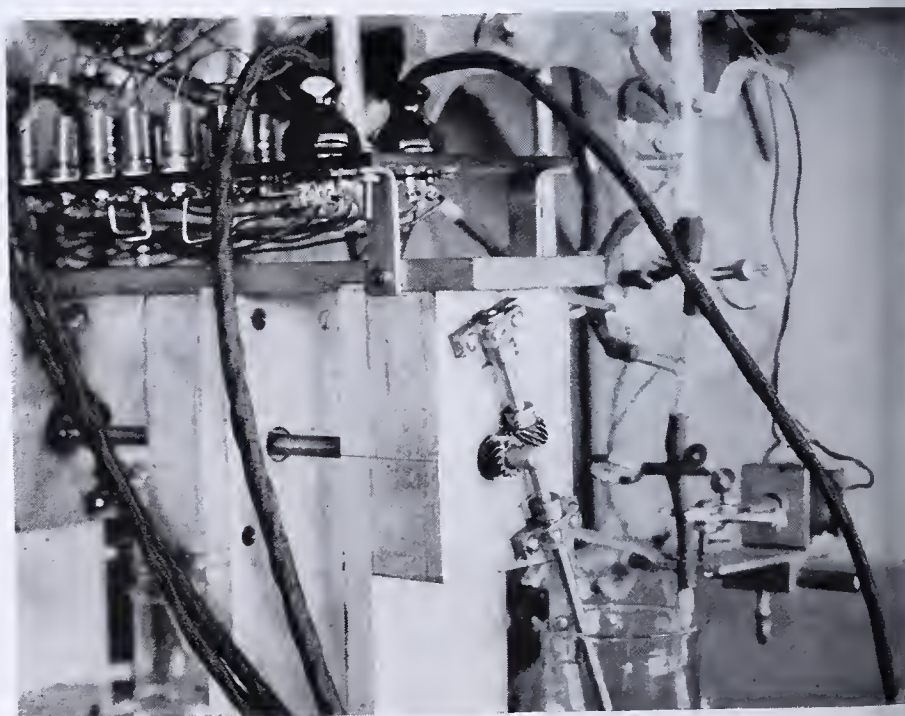


FIGURE 4. CLOSE-UP VIEW OF TITRATION ASSEMBLY

flow of reagent is stopped by turning on the alternating power again, since the solenoid buret clamps close when the solenoid is energized, and the galvanometer deflections of the 10 samples are again observed by means of the automatic switching arrangement. If none of the titrations is yet near the end point, the above procedure is repeated until one or more are practically at, or have reached an end point, as indicated by a very feeble or zero galvanometer deflection. The process is then continued by controlling the flow of acid to each cell by means of the corresponding toggle switch, *G*, until all titrations have reached



an end point. This is accomplished by alternately adding reagent to the respective cells and observing the cycle of galvanometer deflections.

Often the last two or three titrations to reach an end point can be observed more conveniently on the auxiliary galvanometer. The connections are made by means of the manual switch, thus eliminating the necessity of waiting for a complete rotation of the automatic switch before each galvanometer reading. When all cells have reached the end point, the burets are read, the second reference electrode is switched into the circuit by means of toggle switch *J*, and the entire procedure is repeated.

Adjacent sample cells—for example, 4 and 5—often require considerably different quantities of reagent to reach an end point. If the first cell should be far removed from the end point and the second one close, the oscillation of the galvanometer needle resulting from the violent deflection caused by cell 4 may be greater than the normal deflection that would be caused by cell 5. This situation can usually be anticipated and is taken care of by disconnecting the cell far removed from the end point, by shutting off the corresponding electrode switch, *C*, as will be indicated by the corresponding green light, *D*. When this is done, cell 4 will cause no galvanometer deflection when contact is made by the automatic switch, and the observation for cell 5 can be made without hindrance.

If several cells are involved, the same procedure can be used, in which case the switches, *C*, corresponding to the cells most distant from the end points are turned off just before the automatic switch would have connected them to the galvanometer.

In case a very complicated situation arises, one cell may be observed on the auxiliary galvanometer, some cells disconnected as described above, and others observed on the main galvanometer. By means of this flexibility in manipulation, the operator can make the necessary galvanometer observations without any great difficulty, regardless of the order in which the end points are reached.

In using the apparatus for other titrations, it might often be more practical to have the reagent added dropwise continuously from the burets, shutting off each titration when the end point was reached. Such a procedure is probably what could be expected normally, on the basis of the description of the apparatus, especially where the approximate amount of reagent cannot be anticipated. However, in the case of fish titrations, where definite minimum titration values are always encountered, experience has shown that the procedure which has been described requires much less time in completing a series.

### Applications

While the apparatus was designed especially for use with fish, there is no reason why it cannot be used for numerous other titrations. It is, of course, of chief value where a large number of similar titrations are being run frequently, and can best be adapted to titrations which are fairly well buffered at the end point. Some possible applications are to the determination of total acidity of various food products, fatty acid determinations in oils, and many titrations where a color standard is used in titrating to a definite *pH* value (Kolthoff and Furman, 2). Other electrode systems than the quinhydrone can be used if a fairly stable *e. m. f.* is rapidly attained. By using the 2 reference electrodes, two different types of titrations can be run simultaneously.

It is also possible to make the apparatus completely automatic, so that the burets are shut off at the end point without manual switch manipulation. This can be done by substituting a controlling potentiometer of suitable sensitivity for the central galvanometer. The output of this potentiometer would have to be connected through the rotary automatic switch to the solenoids on the burets. However, such

an arrangement would greatly complicate the apparatus and add considerably to the cost.

The total expenditure for parts for constructing the apparatus as described, including the automatic buret shut-offs but not the burets, stirrers, beaker supports, or electrodes, is about \$175. A considerable portion of the equipment, such as the jeweled pilot lights, the step-down transformer for the lights, the toggle switches, etc., are standard radio parts, obtainable at most radio supply stores.

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## CORRESPONDENCE

### Standardization of 2,6-Dichlorophenolindophenol for Ascorbic Acid Titration

SIR: Two papers appeared simultaneously in the ANALYTICAL EDITION (1, 3) purporting to disclose a new method for the standardization of the redox indicator 2,6-dichlorophenolindophenol. An editor's note draws attention to the coincidence that Menaker and Guerrant publish their "improved method" virtually at the same time as the "new method" of Buck and Ritchie, and states that "priority for the published disclosure must be given to Buck and Ritchie."

Actually, this method (wherein the indophenol is caused to oxidize potassium iodide to free iodine which is then titrated with thiosulfate) was published several years ago (4) and appears to have been put forward by Dick (2) who was an associate of Tillmans. It is evident, therefore, that this method—which we have found to be thoroughly reliable—should be credited to Dick and not to the authors of either of the recent papers (1, 3).

For a comparison of details, the directions given in the earlier publication (4) may be worth noting: "To 10 ml. of dye solution add 3 ml. of fresh 10 per cent potassium iodide solution and 2 ml. of 32 per cent sulfuric acid, mixing carefully until the blue color has changed completely through red to yellow; add 60 ml. of water and titrate with 0.01 *N* thiosulfate." It will be seen from this that Dick's method is practically identical with those referred to above.

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# MICROCHEMISTRY



## Qualitative Separations on a Micro Scale

Analysis of the Tellurium and Copper Groups of A. A. Noyes and W. C. Bray

BERL S. ALSTODT AND A. A. BENEDETTI-PICHLER, New York University, New York, N. Y.

A milligram procedure is presented for the analysis of the tellurium and copper groups of A. A. Noyes and W. C. Bray. The scheme provides for the isolation, estimation, and confirmation of 10 micrograms of any member of the groups in the presence of 500 micrograms of any other member. The essential features of the scheme of Noyes and Bray are retained.

Rhodium is precipitated by titanous chloride as metallic rhodium, redissolved, and confirmed by the red coloration obtained with stannous chloride. Molybdenum is identified by the blue coloration of the residue of the ether extract, the red coloration produced by potassium thiocyanate, and the precipitation of the black sulfide. The presence of other elements of the two groups is confirmed by slide tests. Examples show the applicability of the procedure.

**I**N THIS study of the tellurium and copper groups, the scheme of Noyes and Bray (17) has been adopted as in previous investigations (1-5, 7, 8). Several changes were made, however, to render the procedure more suitable for the handling of small quantities of material. The working technique employed was that developed by Emich as described by Benedetti-Pichler and Spikes (6). Rachele's pressure cap for microcones (3) was used for heating under pressure.

The precipitation of the combined tellurium and copper groups is performed by heating under pressure with hydrogen sulfide. If iridium or molybdenum is suspected, the centrifugate from the hydrogen sulfide precipitate is evaporated to a small volume, made approximately 4 molar in hydrochloric acid, saturated with hydrogen sulfide, and again heated under pressure. This treatment is necessary for a sufficiently complete precipitation of the sulfides of iridium and molybdenum.

The analysis of the tellurium group, comprising tellurium, molybdenum, iridium, and rhodium, requires the exercise of special care to assure satisfactory recoveries of the two last-named metals. First, any selenium which might still be present is removed by saturating the strongly acid solution with sulfur dioxide. The solution is then made approximately 2.7 molar in hydrochloric acid for the precipitation

of the tellurium, and the treatment with sulfur dioxide repeated. No iridium is precipitated under these conditions. Scott (18) and McAlpine and Soule (15) claim that metallic iridium is precipitated by sulfur dioxide from hot solution but Fresenius (10) states that sulfur dioxide does not precipitate iridium from solutions of iridic chloride. The latter statement was confirmed by the authors' experiments. Solutions of various amounts of iridic chloride in 12 molar hydrochloric acid, 2.7 molar hydrochloric acid, and water were saturated with sulfur dioxide and heated under pressure. In none of the tests was a precipitate observed, although reduction from the iridic to the iridous state seems to take place as is indicated by the change of color. In experiments dealing with the precipitation of tellurium from solutions containing large quantities of iridium, no indication of a coprecipitation of the latter element was obtained.

On the gram scale, the black precipitate of tellurium serves as a confirmatory test. In microprocedures, however, some extraneous material may be introduced in the various treatments and assume the appearance of elementary tellurium. An additional confirmatory test appeared advisable and the slide test described by Short (19) has been adopted for this purpose.

Hillebrand and Lundell (13), listing the behavior of chlorides in the "ether extraction method", state that 5 per cent of the iridium is extracted as iridic chloride. Experience has shown that the amount extracted cannot be neglected in qualitative analysis. It, therefore, becomes necessary to avoid the use of excessive volumes of ether and to wash the ether extract for the recovery of iridium. The washing must be saved, and not be discarded as directed by Noyes and Bray. Fortunately, the scheme of these authors removes a large amount of the molybdenum together with the tungsten group and not much ether is required for the extraction of the rest of the molybdenum in the tellurium group.

The metals of the copper group are separated from iridium and rhodium by precipitation as hydroxides. Whenever the precipitate is voluminous, double precipitation becomes necessary for the quantitative collection of the two platinum metals in the filtrate. Iridium and rhodium are finally precipitated as dioxides. For this purpose it was considered advisable to use a procedure resulting from a combination of the modified methods of Noyes and Bray (17) and of Christ (12). These authors use bromine and sodium carbonate—or bromate and bicarbonate—for the simultaneous



precipitation of the dioxides of the platinum metals. It was found, however, that bromate is not well suited for the precipitation of iridium while the use of bromine diminishes the delicacy of the precipitation of rhodium. Therefore, the two methods were combined so as first to precipitate the rhodium by bromate and bicarbonate. Some iridium is precipitated with the rhodium; the balance of the iridium is then precipitated in the filtrate by adding bromine and sufficient sodium carbonate to maintain a pH of approximately 7.5.

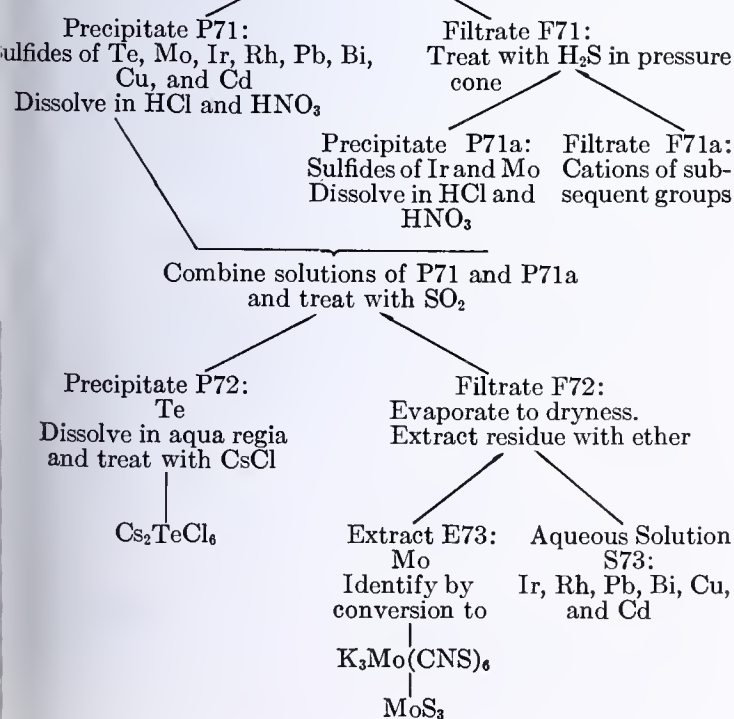
When working with large quantities, the separation of black ammonium chloroiridate is sufficient proof of the presence of iridium. An additional confirmatory test appeared desirable for work on a micro scale, and the test described by Cole (9) was adopted. The octahedra and crosses obtained with hexamethylenetetramine are reddish brown and not colorless, as might be inferred from the table of Mitchell (16); however, sometimes the crystals become colorless on standing. This may be caused by a process of reduction as the reddish brown octahedra rapidly undergo the same change when exposed to sulfur dioxide. The precipitate is also described by Geilmann, and crystals are shown on plate 39 of his atlas (11).

For isolation and estimation, rhodium is precipitated as the metal by addition of titanous chloride (20). This procedure appeared more efficient than the precipitation of chloropentammino rhodium chloride. The solution of the metallic rhodium for the subsequent confirmatory test is performed by heating under pressure with hydrochloric acid and chlorine. The treatment with sulfuric and nitric acids on a hot plate, as recommended by Gilchrist (12), is not practical when working in a microcone. The rhodium is confirmed by the addition of stannous chloride and heating (14). The intensity of the red coloration obtained is obviously dependent upon the quantity of rhodium.

The method of Gilchrist for the separation of rhodium and iridium, consisting of precipitation of metallic rhodium by titanous chloride, removal of the excess reagent with cupferron, and precipitation of iridium dioxide with bromate and bicarbonate, presents various difficulties when applied on a small scale.

### Isolation of Tellurium and Molybdenum

Evaporate filtrate F61 from thallium group to dryness; dissolve residue in hydrochloric acid and treat solution with  $H_2S$



**PRECIPITATION WITH HYDROGEN SULFIDE.** Filtrate F61 from the bromides of the thallium group is treated with 3 cu. mm. of 3 molar ammonium chloride solution and then evaporated to dryness on a steam bath. To the residue are added 15 cu. mm. of 2 *M* hydrochloric acid and 15 cu. mm. of water. The mixture is warmed to hasten solution, and saturated with hydrogen sulfide while warm. After addition of 70 cu. mm. of water, the mixture is again saturated with hydrogen sulfide, and then heated under pressure for 15 minutes in a steam bath. After cooling, the mixture is centrifuged, the supernatant solution is saturated with hydrogen sulfide, and then the heating under pressure in the steam bath is continued for 10 minutes. Solution and precipitate are finally separated with the use of a centrifuge. Precipitate P71 is washed with 10 cu. mm. of hot water, and the washing is added to centrifugate F71.

If iridium or molybdenum is expected to be present, centrifugate F71 is evaporated to approximately 10 cu. mm., treated with 20 cu. mm. of 6 *M* hydrochloric acid, heated on a steam bath for 10 minutes, saturated with hydrogen sulfide, and heated under pressure in a boiling water bath for one-half hour. After cooling, the solution is saturated again with hydrogen sulfide, and heated for another half hour under pressure in the steam bath. If any precipitate P71a is obtained, the mixture is cooled and centrifuged, the supernatant liquid is removed, and the precipitate is washed with 5 to 10 cu. mm. of hot water. The washings are rejected. Centrifugate F71a contains the cations of the subsequent groups.

**SOLUTION OF SULFIDES AND ISOLATION AND ESTIMATION OF TELLURIUM.** Precipitate P71 is treated with 20 to 40 cu. mm. of 12 *M* hydrochloric acid, and the mixture is heated on a steam bath for 5 minutes. Then 4 to 8 cu. mm. of 16 *M* nitric acid are added, and the mixture is heated at 70°C. until the precipitate is dissolved.

If a precipitate P71a has been obtained, it is treated with 5 to 10 cu. mm. of 12 *M* hydrochloric acid and heated on the steam bath for 5 minutes. Then 1 to 2 cu. mm. of 16 *M* nitric acid are added and the mixture is warmed at 70°C. until the precipitate is dissolved. The solution is transferred to the solution of P71, and two 10-cu. mm. portions of 12 *M* hydrochloric acid are used to make the transfer quantitative.

The solution of precipitate P71, or the combined solutions of P71 and P71a, are evaporated to dryness on a steam bath. The residue is dissolved in 10 to 20 cu. mm. of 12 *M* hydrochloric acid and the solution is saturated with sulfur dioxide. Any selenium which remained behind from the distillation of the selenium group will precipitate at this time, and be removed from the solution. For the precipitation of the tellurium, the solution is then diluted with such a volume of water—35 to 70 cu. mm.—as to make the mixture approximately 2.7 molar in hydrochloric acid. The mixture is then saturated with sulfur dioxide and heated under pressure in a steam bath for 15 minutes. After centrifuging, supernatant liquid F72 is transferred to another microcone while still hot. Precipitate P72 is washed with two 10-cu. mm. portions of hot water and the washings are added to filtrate F72. The volume of the tellurium precipitate is compared with that of a precipitate obtained from a tellurium solution of known content.

**CONFIRMATORY TEST FOR TELLURIUM.** Precipitate P72 is heated with 5 to 10 cu. mm. of aqua regia; the resulting mixture is centrifuged, and the clear solution transferred to a slide and evaporated to dryness. The residue is dissolved in 5 cu. mm. of 2 *M* hydrochloric acid, approximately 0.5 cu. mm. of solid cesium chloride is added to the solution, and the test is examined under the microscope. Lemon-yellow hexagons and triangles of cesium chlorotellurite confirm the presence of tellurium. When now a crystal of potassium iodide of approximately 0.1-cu. mm. volume is added to the test drop, the yellow crystals become brownish, and with more potassium iodide amorphous brown grains result.

**ISOLATION OF MOLYBDENUM.** Filtrate F72 is evaporated to dryness on a steam bath, and 1 cu. mm. of 16 *M* nitric acid is added to the residue. The evaporation to dryness is repeated. After cooling, 5 cu. mm. of 6 *M* hydrochloric acid are added to the residue, and the resulting solution is extracted with three portions of approximately 50 cu. mm. of ethyl ether. The ether extracts are collected in a centrifuge cone and washed once with 5 cu. mm. of 6 *M* hydrochloric acid. The washing, which may contain iridium, is added to aqueous solution S73.

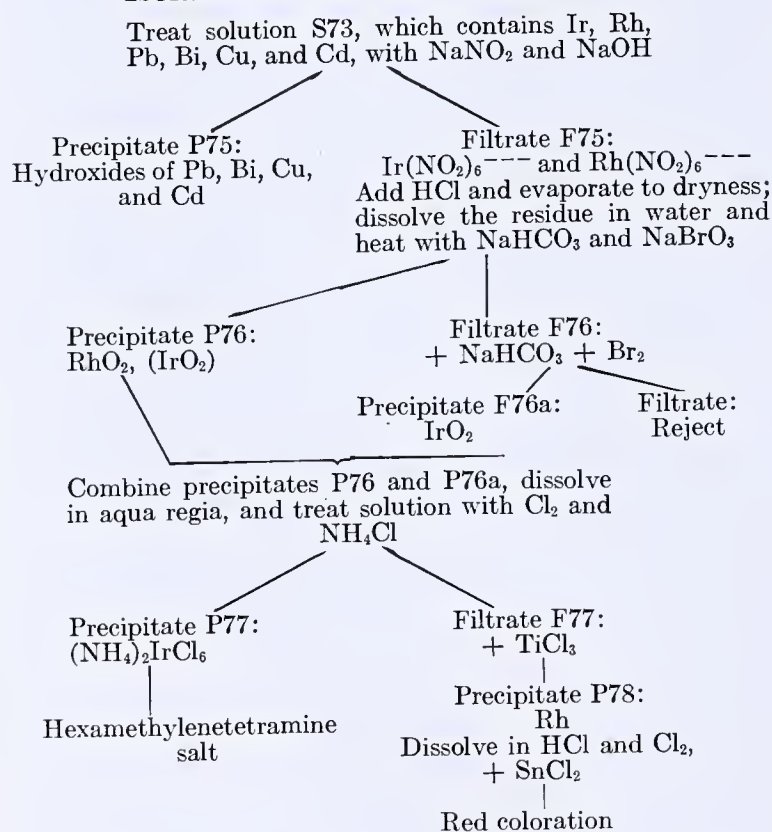
**IDENTIFICATION OF MOLYBDENUM.** Washed ether extract E73 is evaporated in the centrifuge cone to dryness. The residue is heated by slowly drawing the point of the cone through a Bunsen flame. The appearance of a blue coloration in the point of the cone indicates the presence of molybdenum. Sometimes, however, this blue coloration fails to appear. In such instances, the coloration will usually appear if the residue is treated with 2 cu. mm. of 6 *M* hydrochloric acid, the acid evaporated, and the residue heated again.



Whatever the result of the foregoing test, the residue is finally dissolved in 2 cu. mm. of 6 *M* hydrochloric acid, and then 12 *M* ammonia is added until the solution becomes ammoniacal. The mixture is stirred and centrifuged. If a precipitate of ferric hydroxide has been obtained, the supernatant solution is transferred to another cone, the precipitate of ferric hydroxide is washed with 5 cu. mm. of 6 *M* ammonia, and the washing is combined with the clear ammoniacal solution, which is heated on a steam bath to remove most of the ammonia. Finally the solution is made just acid by adding small portions of 6 *M* hydrochloric acid. Now 2 cu. mm. more of the acid, 5 cu. mm. of water, and 5 cu. mm. of 1 *M* potassium thiocyanate solution are added. In the presence of molybdenum the solution becomes yellow. The mixture is stirred after adding a kernel of metallic zinc of about 0.1-cu. mm. volume. When the stirring is continued for 1 to 2 minutes, the appearance of a cherry-red coloration confirms the presence of molybdenum. The coloration fades in a few minutes and is not suited for estimation of the quantity of molybdenum.

**ESTIMATION OF MOLYBDENUM.** The solution is separated from the metallic zinc, the metal is washed with 5 cu. mm. of water, and the washing is combined with the solution. The latter is treated with 1 cu. mm. of 12 *M* hydrochloric acid, saturated with hydrogen sulfide, and heated under pressure in the steam bath for 10 to 20 minutes. The volume of the precipitate of molybdenum sulfide is compared with that of a precipitate obtained from a known quantity of molybdenum.

### Isolation of Rhodium and Iridium



**SEPARATION OF COPPER GROUP FROM IRIIDIUM AND RHODIUM.** Solution S73 is first warmed to remove the dissolved ether, and then evaporated just to dryness on the steam bath. The residue<sup>1</sup> is dissolved in 1 cu. mm. of 6 *M* acetic acid and 10 cu. mm. of water; the solution is treated with 5 cu. mm. of 3 *M* sodium nitrite solution and warmed at 60° to 70° C. for 5 minutes. After cooling, and without filtering, 1-cu. mm. portions of 3 *M* sodium hydroxide solution are added with stirring until the mixture is alkaline to litmus paper. If the hydroxide precipitate is voluminous, the mixture may be diluted with 10 to 20 cu. mm. of water during neutralization. After centrifuging, precipitate and solution are separated, and the precipitate is washed with 5 to 10 cu. mm. of hot water; the washing is added to the centrifugate. Filtrate F75 is finally treated with 5 cu. mm. of 1 *M* sodium bicarbonate solution, and, if a precipitate

forms, it is collected with the use of the centrifuge and combined with precipitate P75.

If precipitate P75 is voluminous, it is dissolved in approximately 10 to 15 cu. mm. of 12 *M* hydrochloric acid, and the solution is evaporated to dryness. The residue is treated with 1 cu. mm. of 6 *M* acetic acid, 10 cu. mm. of water, and 3 cu. mm. of 3 *M* sodium nitrite solution, and the mixture is precipitated with 3 *M* sodium hydroxide as described above. The centrifugate now obtained is added to filtrate F75, and the precipitate is considered as P75.

**PRECIPITATION OF DIOXIDES OF IRIIDIUM AND RHODIUM.** Filtrate F75 is treated with 5 cu. mm. of 12 *M* hydrochloric acid and evaporated just to dryness. The residue is dissolved by adding 15 cu. mm. of water and heating on a steam bath for 5 minutes. Then 20 cu. mm. of 10 per cent sodium bromate solution are added, and sufficient filtered 1 *M* sodium bicarbonate solution to render the mixture alkaline. The mixture is then heated on a steam bath for 20 minutes. The separation of a green precipitate indicates the presence of rhodium. The contents of the microcone are centrifuged, and the supernatant clear solution is transferred to another cone. The precipitate is washed with 10 cu. mm. of hot water, and the washing is added to the centrifugate.

A minute drop of bromine is added to filtrate F76. The reaction of the mixture is tested by means of nitrazine paper, and the pH is adjusted to approximately 7.5 by the addition of 1 *M* sodium bicarbonate solution. The mixture is then heated on the steam bath for 20 to 30 minutes. A bluish black precipitate indicates the presence of iridium. Precipitate P76a and the solution are separated, and the latter is rejected. The precipitate is washed with 5 cu. mm. of hot water.

**ISOLATION AND ESTIMATION OF IRIIDIUM.** Precipitates P76 and P76a, the first mainly consisting of rhodium dioxide and the second mainly of iridium dioxide, are combined as follows. Precipitate P76a is dissolved in a mixture of 6 cu. mm. of 12 *M* hydrochloric acid and 2 cu. mm. of 16 *M* nitric acid. The solution is transferred to precipitate P76, and the mixture is warmed until P76 has completely dissolved. The cone which contained P76a is rinsed with two 8-cu. mm. portions of a mixture of three volumes of 12 *M* hydrochloric acid and one volume of 16 *M* nitric acid, and the washings are added to the solution of the combined precipitates.

The solution of the combined precipitates P76 and P76a evaporated to dryness on a steam bath, the residue is treated with 1 to 2 cu. mm. of 6 *M* hydrochloric acid, and the mixture again evaporated to dryness. The residue is dissolved in approximately 1 cu. mm. of 6 *M* hydrochloric acid and 3 to 5 cu. mm. of water. The solution is saturated with chlorine and warmed at 50° C. for 5 minutes. Solid ammonium chloride is then added until the solution appears saturated with this salt. A large excess—more than one or two crystals—of solid ammonium chloride must be avoided. The mixture is heated on the steam bath for 15 minutes, allowed to cool, again saturated with chlorine, and allowed to stand for 0.5 hour. Any ammonium chloride, which may have separated out, is now dissolved by adding water in cubic millimeter portions, and the black precipitate of ammonium chloroiridate is collected in the point of the cone by means of the centrifuge. Centrifugate F77 is transferred to another cone, and the precipitate is washed with 5 cu. mm. of 3 *M* ammonium chloride solution. The washing is added to filtrate F77. The volume of precipitate P77 is compared with that of ammonium chloroiridate obtained with a known amount of iridium.

**CONFIRMATORY TEST FOR IRIIDIUM.** Precipitate P77 is dissolved in 5 to 10 cu. mm. of water, warming if necessary; a drop of the solution is transferred to a microscope slide and treated with a kernel of hexamethylenetetramine of approximately 0.1 cu. mm. volume. The separation of reddish brown octahedra and crosses confirms the presence of iridium.

**ISOLATION AND ESTIMATION OF RHODIUM.** Filtrate F77 is evaporated to dryness, and the residue is treated with 2 cu. mm. of 18 *M* sulfuric acid and 40 cu. mm. of water. The mixture is heated on the steam bath for 5 minutes, after which a very slight excess of a 15 per cent solution of titanous chloride is added, and the heating on the steam bath is continued for 1 to 2 minutes. A precipitate of black metallic rhodium is collected in the point of the cone, and the supernatant solution is removed at once and rejected. Precipitate P78 is washed with 10 cu. mm. of 0.4 *M* sulfuric acid, and the volume of the precipitate is compared with that of a known quantity of metallic rhodium similarly precipitated.

**CONFIRMATORY TEST FOR RHODIUM.** Precipitate P78 is treated with 15 to 30 cu. mm. of 12 *M* hydrochloric acid. The mixture is saturated with chlorine, and, if necessary, heat under pressure on a steam bath until the precipitate is dissolved. If complete solution is not obtained after heating for seven

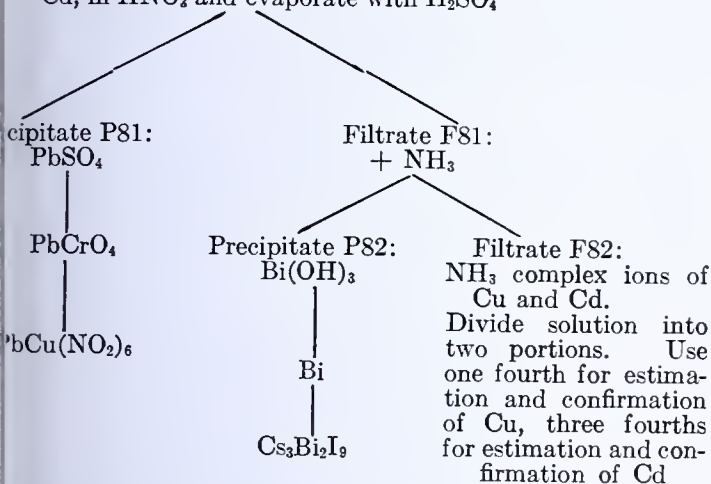
<sup>1</sup> A blue coloration of this residue indicates incomplete separation of the molybdenum. It is then necessary to repeat the extraction with ether as described above. Since most of the molybdenum is removed with the tungsten group and the small quantities found in the tellurium group are readily extracted by ether, molybdenum will rarely be present at this stage of the analysis.



minutes, the supernatant solution is removed from the metal and transferred to another cone. The residue is treated with another portion of 15 to 30 cu. mm. of 12 M hydrochloric acid, and the treatment with chlorine and the heating under pressure is repeated as described above. The resulting solutions of rhodium are combined and freed by centrifuging from any white precipitate which may appear at this stage whenever too large an excess of titanous chloride is used in the precipitation of the metallic rhodium. The clear solution of rhodium is evaporated to a volume of approximately 5 cu. mm. and then taken up into a capillary. The cone used in the concentration of the rhodium solution is rinsed with 3 to 5 cu. mm. of stannous chloride reagent, which is then also taken up into the capillary. The capillary is sealed at both ends, its contents are mixed, and the capillary is finally placed for 5 minutes in boiling water. The appearance of a yellowish red to deep red coloration in the capillary confirms the presence of rhodium.

### Analysis of the Copper Group

Dissolve precipitate P75, which may contain hydroxides of Pb, Bi, Cu, and Cd, in HNO<sub>3</sub> and evaporate with H<sub>2</sub>SO<sub>4</sub>



**SOLUTION AND ESTIMATION OF LEAD.** Precipitate P75 of hydroxides of the copper group is dissolved in 5 to 10 cu. mm. of 6 M nitric acid. To the clear solution are added 3 cu. mm. of 8 M sulfuric acid, and the mixture is evaporated on the steam bath to a volume of approximately 3 cu. mm. This evaporation, which is carried out to eliminate the nitric acid, is accomplished gradually by blowing air through the cone. After cooling, the residue is diluted with 10 cu. mm. of water, and the mixture is stirred and then allowed to stand for 3 minutes. The contents of the cone are centrifuged, and the volume of precipitate P81 compared with that of a lead sulfate precipitate obtained from a known quantity of lead. Centrifugate F81 is transferred to another cone; the precipitate is washed first with 3 to 5 cu. mm. of 6 M sulfuric acid and then with 3 to 5 cu. mm. of cold water. Washings are added to centrifugate F81.

**CONFIRMATORY TEST FOR LEAD.** Precipitate P81 of lead is either used for a triple nitrite test (6), or is dissolved in 10 cu. mm. of 3 M ammonium acetate solution, warming necessary, and precipitated by the addition of 1 cu. mm. of 5 M solution of potassium chromate. The precipitation of lead chromate may be performed in a capillary, or in a cone with a cylindrical tip (8), and the volume of the lead chromate may be used for the estimation of the quantity of lead. It is also possible to subject the chromate precipitate to the triple test.

**SOLUTION, CONFIRMATION, AND ESTIMATION OF BISMUTH.** Filtrate F81 from the lead sulfate is made distinctly ammoniacal by the addition of 20 cu. mm. of 6 M ammonia. The mixture is centrifuged, the supernatant solution transferred to another cone, and the precipitate washed with 5 cu. mm. of hot water. A washing is added to centrifugate F82. Precipitate P82 of bismuth hydroxide is treated with 5 to 10 cu. mm. of freshly prepared (6) sodium stannite reagent, and the contents of the cone are mixed and centrifuged. The volume of the black precipitate of metallic bismuth is used for the estimation of the quantity of this metal. The black precipitate is finally washed with two 10-cu. mm. portions of hot water, and then dissolved in 5 cu. mm. of 16 M nitric acid. A drop of this solution is transferred to a slide, evaporated to dryness, the residue dissolved in 2 M nitric acid, and this solution used for the precipitation of the cesium iodobismuthite or the bismuth cobaltite (6).

**THE DETECTION AND ESTIMATION OF COPPER AND CADMIUM** have been described in former publications (6). The copper is

usually recognized by the blue coloration of the ammoniacal solution, and the estimation of copper is based on the colorimetric evaluation of the intensity of the coloration. If a further confirmatory test for copper is desired, one fourth of filtrate F82 is taken up with a capillary tube and treated with 1 cu. mm. of 6 M acetic acid and 1 to 2 cu. mm. of 0.25 M potassium ferrocyanide. The capillary is sealed at both ends and its contents are mixed by centrifuging and then allowed to stand for 2 to 3 minutes. The reddish brown precipitate of cupric ferrocyanide can then be collected at one end of the capillary by means of the centrifuge. The clear solution may be removed, and the precipitate washed with 5 cu. mm. of hot water and dissolved in 5 to 10 cu. mm. of 6 M nitric acid. Transference of this solution to a slide, evaporation to dryness, solution of the residue in 2 M nitric acid, and treatment with potassium-mercuric thiocyanate furnish the characteristic crystals of copper-mercuric thiocyanate.

### Limitations of the Scheme

The range of applicability of this scheme of analysis may be seen from Table I, which shows the results obtained in the analyses of solutions of various composition. The quantities recovered represent averages derived from the results of several experiments. All the estimations were performed with the use of microcones with cylindrical tip (8). The compositions of solutions X and Y were unknown to the analyst. The small amount of lead found in the analysis of X was introduced as an impurity of the copper salt used in the preparation of solution X.

TABLE I. ANALYSES OF SOLUTIONS OF KNOWN COMPOSITION

Solution	Number of Analyses	Composition Found Micrograms	Actual Composition Micrograms
A	2	10 Te, 10 Mo, 9 Ir, 9 Rh	10 of each
B	2	9 Pb, 8 Bi, 10 Cu, 7 Cd	10 of each
C	12	19 Te, 18 Mo, 15 Ir, 15 Rh, 17 Cu	20 of each
D	5	18 Te, 18 Mo, 13 Ir, 14 Rh	20 of each
E	3	14 Pb, 14 Bi, 17 Cu, 11 Cd	20 of each
F	3	10 Te, 9 Mo, 7 Ir, 8 Rh	10 of each
G	2	7 Pb, 7 Bi, 8 Cu, 6 Cd	10 of each
H	4	10 Te, 9 Mo, 7 Ir, 8 Rh	10 of each
I	5	14 Pb, 12 Bi, 16 Cu, 10 Cd	20 of each
J	5	10 Te, 9 Mo, 7 Ir, 7 Rh	10 of each
K	1	38 Pb, 33 Bi, 40 Cu, 25 Cd	50 of each
L	2	10 Te, 9 Mo, 6 Ir, 7 Rh	10 of each
N	1	75 Pb, 70 Bi, 85 Cu, 60 Cd	100 of each
Y	1	9 Te, 9 Mo, 5 Ir, 6 Rh	10 of each
		100 Pb, 100 Bi, 120 Cu, 90 Cd	150 of each
		9 Te, 8 Mo, 3 Ir, 4 Rh	10 of each
		Not analyzed for Pb, Bi, Cu, Cd	200 of each
		9 Te, 7 Mo, trace Ir, 2 Rh	10 of each
		Not analyzed for Pb, Bi, Cu, Cd	500 of each
		135 Te, 120 Mo, 120 Ir, 120 Rh	150 of each
		6 Pb, 6 Bi, 7 Cu, 5 Cd	10 of each
		150 Ir, 150 Rh, 4 Pb, 120 Cu	100 Ir, 200 Rh, 200 Cu
		100 Te, 140 Mo, 120 Pb	100 Te, 200 Mo, 200 Pb

The various limiting proportions have not been determined in the exact sense. However, no difficulties were experienced in detecting 10 micrograms of any element in the presence of 500 micrograms of any other element of the copper and tellurium groups.

### Acknowledgment

The authors are indebted to the authorities of the Brooklyn College of Pharmacy for permission to use their laboratory facilities.

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# Pregl Sulfur Combustion of Metallic Compound

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THE only limitation to the excellent Pregl catalytic combustion method for sulfur is its lack of applicability to compounds which contain a metal (1). As these occur frequently, an attempt was made to modify the method to include them.

As a few preliminary experiments showed that the residue from this type of substance contained a considerable amount of metallic sulfate, attempts were made to prevent its formation or to decompose it when formed. The substitution of a porcelain boat to avoid the catalytic effect of platinum did not prevent its formation, and the addition of various substances, such as potassium dichromate, chromium trioxide, sodium peroxide, and cupric nitrate, to the sample did not leave the residue sulfate-free.

As it seemed probable that the formation of sulfate could not be avoided under the conditions of the determination, it was decided that the solution of the problem depended on treatment of the combustion products to obtain the theoretical yield of barium sulfate. While only a comparatively few compounds were readily available, their metals belonged to four of the five qualitative groups and possessed widely different chemical behavior.

This treatment ensures the quantitative transfer of sulfate with the minimum amount of solvent. In the case of the barium compound, the transfer of the residue to the crucible was accomplished by overturning the boat and spraying vigorously from the wash bottle to remove the last traces of residue. Other barium compounds, if present, are dissolved by the acid, leaving only the insoluble sulfate. Insoluble residues of other metals must be extracted by boiling gently with 0.1 N hydrochloric acid and treating the extract with barium chloride in the usual manner. Chromium residues contain no sulfate (Table I) and subsequent treatment of the residue is unnecessary.

TABLE II. YIELD OF BARIUM SULFATE  
(Separate treatment of residue omitted)

Compound	Sample Mg.	BaSO <sub>4</sub>		Sulfur	
		Found Mg.	Calcd. Mg.	Found %	Calcd. %
Lithium cystinate	5.324	9.81	9.85	25.32	25.40
Barium cystinate	5.840	7.22	7.25	16.98	17.04
Copper cystinate	5.500	8.47	7.49	21.15	21.21
Sodium β-naphthoquinone sulfonate	6.904	6.17	6.19	12.29	12.31

## Discussion

The residue and the contents of the spiral were treated separately, as shown in Table I, to show the yields of barium sulfate. Table I shows the results when the separate treatment of the residue is omitted. The acid-soluble residues are placed in the weighed crucible and dissolved by means of the acid washings of the spiral contents. The total sulfate is collected and treated with barium chloride in the usual fashion. When insoluble residues other than barium are formed, the hydrochloric acid extract can be added to the partly evaporated contents of the spiral previously placed in the weighed crucible. In this manner accurate results can be obtained.

## Acknowledgment

The author is indebted to G. Toennies of the Lankenau Hospital, Philadelphia, for the lithium and barium salts used in this work.

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## Experimental

The substances were run according to Pregl's method (2, 3), as modified by Saschek (4). The contents of the spiral were treated in the usual manner and the weights of barium sulfate recorded. The residues left in the boat were weighed, but, owing to the variable amounts of sulfur and metal present in the sample, did not conform to the weight demanded by the pure sulfate. This indicated that the oxide or carbonate was formed in addition to the sulfate, and the weights were therefore disregarded as of no significance.

The acid-soluble residues, which included all but the barium derivative, were transferred to another weighed crucible and dissolved in 7 to 10 ml. of 0.1 N hydrochloric acid, and the boat was rinsed with hydrochloric acid (1 to 200) from a wash bottle.





## RESEARCH LABORATORY OF THE NATIONAL LEAD COMPANY—TITANIUM DIVISION

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THE Research Laboratory of the National Lead Company—Titanium Division (Titanium Pigment Corporation) transferred from an old building in Brooklyn, N. Y., to a new building specially provided for it in Sayreville, N. J., in 1935. The laboratory was designed under the supervision of J. L. Turner, director of research. Additions to the laboratory facilities made necessary by expansion of the research work were completed in 1938. This laboratory is devoted to the chemistry and technology of titanium, with particular emphasis upon the titanium pigments. This specialized field of chemical engineering and applied science required certain features in design and construction which are not common to all research laboratories. The laboratories have been designed to permit the investigation of any problem using quantities of materials from purely theoretical to full laboratory scale to large-scale laboratory and finally to pilot-plant-scale amounts. The basic plan of the research laboratories proper was intended to furnish an individual laboratory for each senior research scientist. The building housing the laboratories is also occupied by administrative, engineering, and accounting offices of the titanium pigment plant of the National Lead Company—Titanium Division. Its architecture is along conservative modern lines, providing a maximum amount of window space. The construction is of reinforced concrete. Exterior walls are brick, floors concrete, and interior walls of hollow tile having a sand-finish cement plaster. The ceilings are made of metal lath with a smooth plaster finish. The side walls above the dado are painted light green and the dado is green, while the ceiling is white. This color combination, in a "Titanox"-C flat paint, is very satisfactory with regard to both illumination and permanence of color. The choice of green paint for the laboratory walls was based upon the desire to obtain high reflectance—i. e., maximum brightness in the rooms—without the glare which might be caused by white walls and at the same time have as little interference as possible with visual grading of the tone of white pigments, which is such an important part of the work of this laboratory. The floors are laid with asphalt-bonded asbestos tile

in red and black, which is giving excellent service in laboratories as well as in offices. Windows are of the casement type in metal frames and are provided with aluminum wire screens and Venetian blinds.

### Layout of Laboratories

The individual laboratories are approximately  $19 \times 19$  feet, although some of the rooms are larger in order to improve their adaptation to certain types of work. Each chemical laboratory is furnished with a wall bench 17 feet long  $\times$  2 feet 6 inches wide and a center table 15 feet long  $\times$  4 feet wide with a sink at one end. A cabinet for storage of reagents and glassware, an illuminated titration table, and a desk and chairs complete the furnishings. The oak furniture is of flush construction throughout, coated with a special acid- and solvent-resistant finish. The sink and table tops are Alberene stone and the drainage system is constructed with Duriron.

The hoods are built of impregnated Transite, each equipped with a separate ventilating fan and duct to the roof. The hoods in the research laboratories are 5 feet long with a 3-foot front opening provided with a glass sash which may be lowered to close the hood entirely if so desired. The over-all height is 5 feet with the top chamfered above the door opening. Exhaust is at the top of the hood only. The fans are of the squirrel-cage type having a speed of 850 revolutions per minute and a free volume delivery of 800 cubic feet per minute. The ducts connecting the fans to the hoods and exhaust ducts are sheet iron homogenized with lead, which has given satisfactory protection against sulfuric acid corrosion. These hoods have proved entirely adequate for the handling of the sulfur trioxide and sulfuric acid fumes which accompany much of the laboratory work. The only maintenance required has been occasional cleaning of the fans, which tend to accumulate ammonium sulfate upon the blades.

Service lines are provided on both the side tables and center tables. These comprise vacuum, compressed air, gas, hot and cold water, steam, and 110-volt alternating and direct current. The useful precaution of having traps



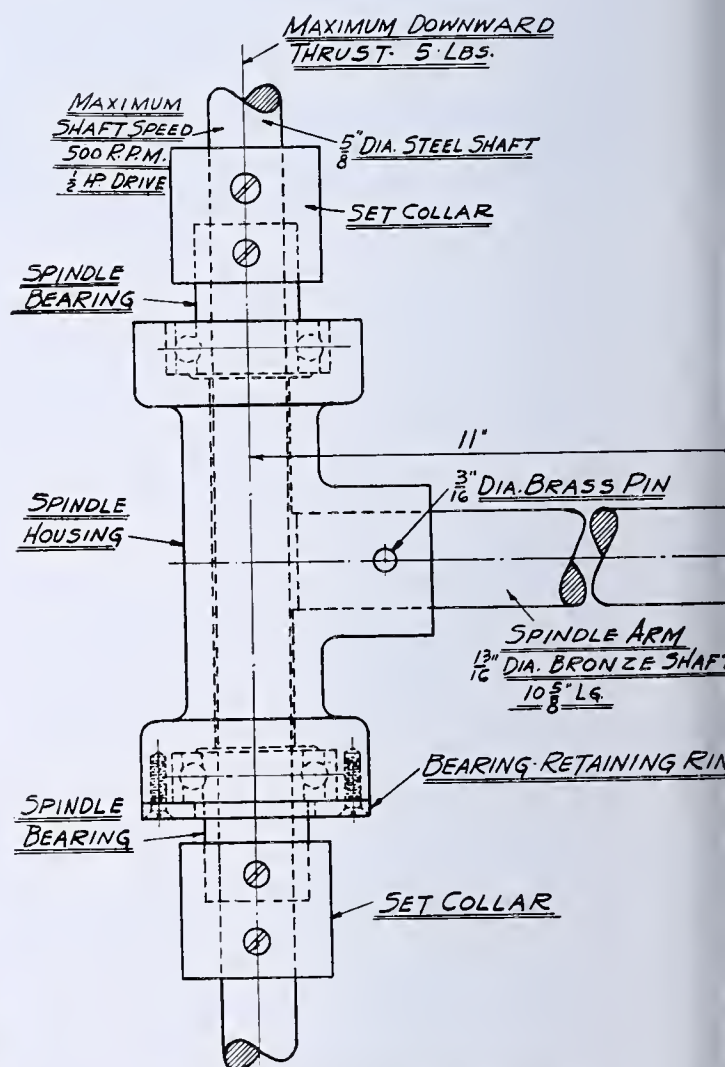
in each laboratory vacuum line has prevented any general stoppage in the main vacuum line and pumps. The traps consist of 4-liter suction-type flasks (without a side opening) placed in the line going to the main service line. This gives an adequate trap for any overflow from the ordinary laboratory suction flasks. The tables contain drain bowls connecting to the sewer. Outlets for 220-volt alternating current are provided in the side walls for any work requiring the higher voltage.

A special feature of each chemical laboratory is the permanently mounted group of stirrers. A line shaft driven by a 0.5-horsepower motor drives a group of four to six stirrer heads by means of belts and pulleys, permitting selection of desired speeds. The shaft is supported in ball-bearing pillow-blocks running in grease. The stirrer head has two thrust bearings to which the stirrer shaft is fastened by means of setscrews. Glass stirrers are usually connected to the stirrer shaft by means of rubber tubing; metal or wood stirrers by means of a collar and setscrews. Permanently mounted black-iron rods between the stirrer heads furnish the supports for the usual clamps and fasteners for holding apparatus. Agitation in apparatus from the size of a 250-ml. beaker or flask to a 5-gallon crock is conveniently accomplished with this setup.

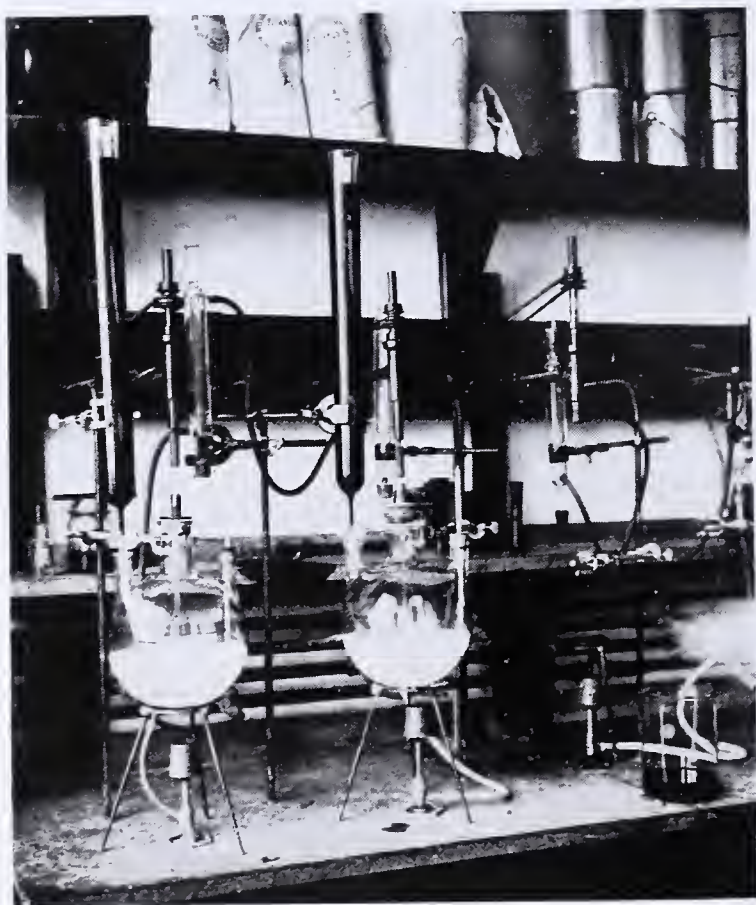
A separate room for all the balances has reduced corrosion and dust problems which had been encountered in the old laboratory where the balances were in the open rooms.

A furnace room with hoods is provided for the various heat treatments and calcining schedules required in pigment research. These hoods also have individual fans to remove the gases and heat from the furnaces. Fans are of the squirrel cage type similar to the smaller hoods but have a speed of 1140 revolutions per minute and a free volume of 2050 cubic feet per minute. Both electric and gas-fired furnaces are used and provide either stationary or rotary calcination. The electric furnaces are automatically controlled. The

control equipment for the furnaces is mounted in the hall outside the furnace room for more convenient observation of the temperatures of the furnaces. By this arrangement the controls also remain at a more nearly constant temperature thereby increasing their accuracy and life. A useful feature of the electrical heating system is the introduction of variable shunt resistance in the furnace circuit for the partial lowering of primary voltage to the transformers. This has greatly reduced the surge usually found when the circuit is completely broken by the automatic control.



SPINDLE BRACKET STIRRER HEADS

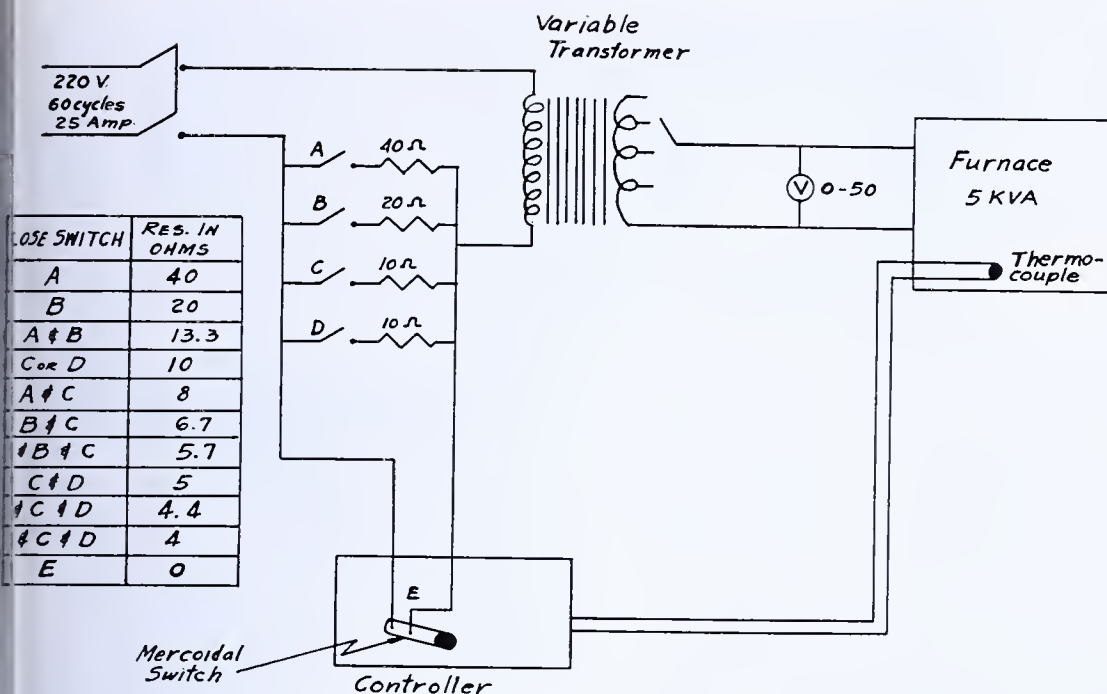


STIRRER ASSEMBLY

The physical laboratory comprises two laboratory rooms, a projection room, and a dark room. Its equipment provides for microscopic examination, testing of brightness, hiding power, and like physical characteristics of pigments and paints. The microscopic equipment is provided with quartz optics as well as glass, so that it is possible to resolve particles to approximately 0.2 to 0.3 micron. Projection of particles on a screen at 8000 to 12,000 diameters allows measurement and counting of fine particles. Centrifuge equipment has been adapted to the problem of the estimation of particles within and below the above ranges by accelerated sedimentation.

The pigment- and paint-testing laboratories were designed for greater flexibility and therefore free-standing tables were used wherever possible. The table tops are covered with stainless steel. Pigment and paint which may have spilled on the surface are easily removed. The tinting strength color laboratory was placed at a northern exposure so as





WIRING DIAGRAM FOR ELECTRIC MUFFLE CONTROL

minute, which maintains the room under a positive static pressure of about 0.5 inch of water. A separate fan is provided for exhausting fumes from the arc. Both fans are placed outside the building in order that they may be serviced without entering the room, and to reduce any vibration and noise to a minimum.

Cooling of the wash water for washing spectrographic plates is provided; water at 10° C. is available. The cooling unit also permits storage of the plates over long periods of time without material change in sensitivity. The cooling unit is an adaptation of a standard water-cooled refrigeration outfit of 0.5-

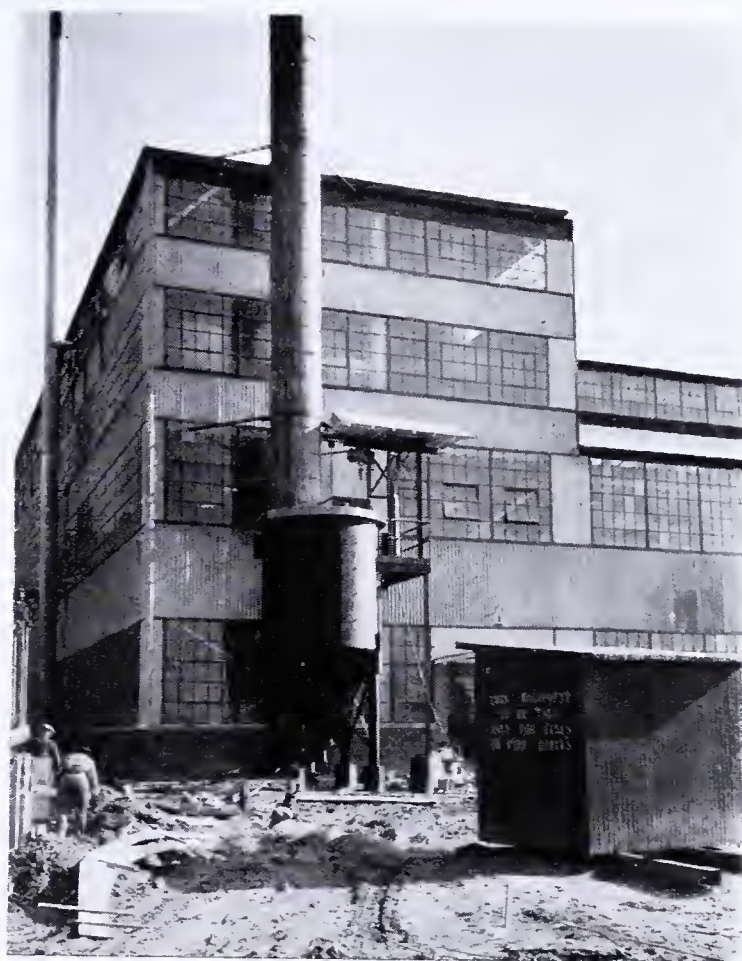
horsepower capacity. The water passes through a 5-gallon tank which is closely wrapped with cooling coils, and has adequate cooling capacity to drop the temperature of water 20° F. at a rate of 20 gallons per hour. The spectrograph is a large Bausch & Lomb Littrow-type instrument. X-ray equipment, in one of the chemical laboratories, finds an important part in the research program of the laboratory.

tain a diffuse light. The installation of filtered air equipment in this and the paint-testing laboratory was found to be desirable in order to lower the dust occurring at a ground level. The paint-testing laboratory is equipped with a roller mill, spray booth, baking oven, and testing apparatus, so that the complete characteristics of a finished pigment or paint may be ascertained in all types of formulations.

A constant-humidity and -temperature room allows the storage of pigments and paints and their examination under controlled conditions if desired. The constant-temperature room is 8 feet wide × 10 feet 6 inches long × 8 feet 6 inches high (inside dimensions). The wall construction is of 4-inch cinder block covered on the outside with 1 inch of plaster and on the inside with 4-inch corkboard and a 0.5-inch covering of cement plaster. The ceiling was formed by sheathing with 0.75-inch matched lumber. Against the sheathing two layers of waterproof insulating paper and one layer of 4-inch corkboard were applied. The ceiling also was sheathed with an inside layer of plaster similar to the side walls. A storage door insulated with 4-inch cork with a fir front and back gives access to the room. A refrigeration compressor with water, sprays, and automatic controllers maintains the desired conditions within the ranges from 40 to 70 per cent relative humidity and 65° to 80° F. dry-bulb temperature with an outside maximum of 95° F. dry-bulb temperature and a minimum relative humidity of 25 per cent. These conditions are maintained within the accuracy and sensitivity of the controller instruments with a supply of 50 cubic feet per minute of outside air into the room.

The rubber laboratory for the study of pigments in rubber is equipped with a roller mill, vulcanizer, etc., and test apparatus so that a complete set of data may be obtained on finished rubber. This laboratory directly concerns itself with the effect of pigment in rubber as a utilization problem.

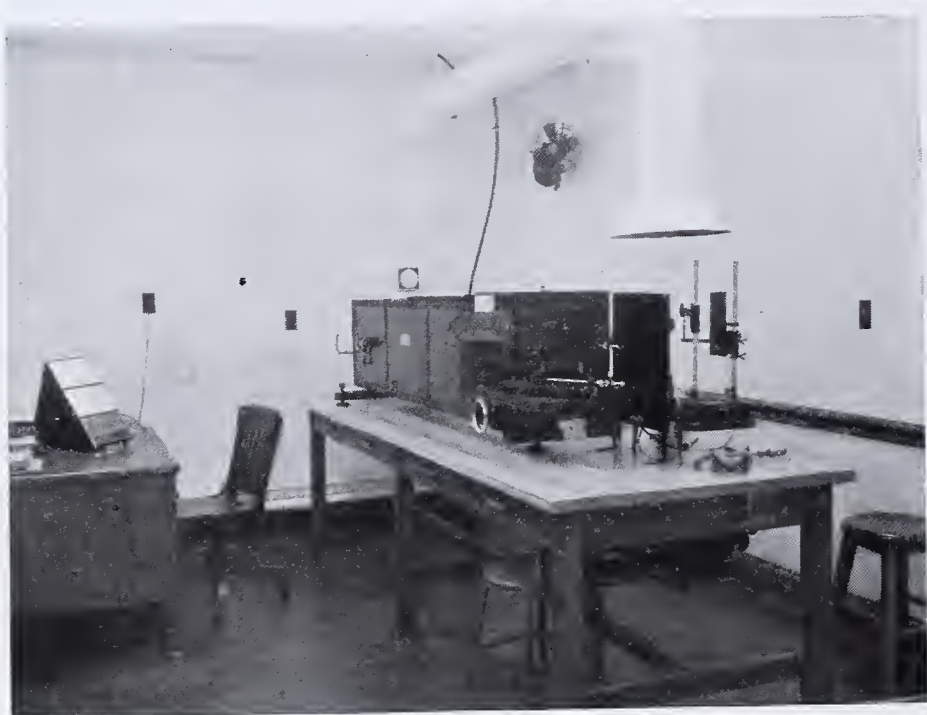
The spectrographic laboratory is of interest, since a dust-free room was required to test the pigments and ores. Air filtration through paper filters has proved adequate with a complete change of air in 6 minutes. The filtration equipment has cooling coils which lower the temperature and humidity in the summer months. The filtration of the air is accomplished with 40 square feet of filter area, using a cellulose-type paper backed up with 10-ounce flannel for final cleaning. The fan to supply air delivers 600 cubic feet per



PILOT PLANT



RIGHT. MUFFLES AND CONTROLS



ABOVE. SPECTROGRAPHIC LABORATORY

RIGHT. TYPICAL RESEARCH LABORATORY



The general laboratory is a laboratory unit for preparation of pigments on a 5-pound scale, before going to semi-pilot-plant scale. The semi-pilot-plant unit, which is in a building of the main plant, will handle 100-pound lots. The pilot plant was designed for production of 1 to 2 tons per day and is a complete pigment plant in a separate building of its own. The preparation of pigment from raw ore to finished pigment can be carried out at the pilot plant, or plant product at any point in the process may be worked up into a final pigment.

A mill room contains a jaw-crusher and a roller mill for the reduction of ores; ball mills, an Aloxite edge-runner mill, and a Raymond laboratory pulverizer are provided for the grinding of pigments.

The library, in a room of its own under the supervision of a trained librarian, necessarily is somewhat limited because of the highly specialized nature of the work of the laboratory. It contains some 500 volumes of books and encyclopedias, about an equal number of volumes of periodicals, 2000 trade catalogs, and 4000 pamphlets, photostats, and reprints. Subscription to 27 current periodicals is maintained.

A stockroom, steam water still, compressor, vacuum pump,

necessary motor generators, and steel storage shelves for samples complete the equipment of the laboratory.

A *bête noire* in the design of laboratories is the choice of service equipment of the required capacity. The following data therefore may be of interest.

The vacuum pump serving all laboratories has a capacity of 9 cubic feet per minute at 29 inches of mercury and is provided with an 80-gallon receiver. It has proved adequate for the laboratory which has a heavy vacuum-filtration load. The compressor delivers 13 cubic feet per minute at 200 pounds per square inch. This pressure is used for paint spray booth service. For the laboratory service lines the pressure is brought down to 25 pounds per square inch by means of a governor. An 80-gallon receiver also is used in connection with the air compressor. The distilled water is obtained from a still delivering 2 to 3 gallons per hour using steam at 30 pounds pressure as the heat source. A 50-gallon chemical stoneware receiver allows adequate storage for the laboratory. The distilled water, chemicals, cylinders, ball mill, etc., are delivered to the other floors by means of a hand-operated dumbwaiter.

The type of layout and the equipment described are proving to be very satisfactory for an inorganic research laboratory with a staff of twenty-six chemists and chemical engineers and twelve nontechnical employees.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Determination of Nitrogen in Stainless Steels

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THE commercial production of chromium steels containing nitrogen has necessitated the development of an accurate method for determining this element. The Allen method (1) for combined nitrogen in plain carbon steels consists in dissolving the sample of metal in the form of drillings or filings in hydrochloric acid (sp. gr. 1.11), making the solution alkaline with calcium oxide, distilling off the ammonia, and completing the determination with Nessler's solution.

Among the authors who have employed modifications of Allen's method are Tschischewski (5), Weiss and Englehardt (2), Ruff and Eisner (4), Johnson (3), and Jordan and Swindell (3). Jordan and Swindell's modification of Allen's

The amounts of nitrogen that were found in the acid-insoluble portions of several stainless steels are shown in Table I. This table also shows that results for nitrogen by the authors' modification of Jordan and Swindell's method agree very well with the results obtained by the vacuum fusion method. The method to be described has been used by this and other laboratories since 1932.

### Method

Five grams of the sample are transferred to a large platinum dish (300-ml.) provided with a tight-fitting cover, and treated with 50 to 60 ml. of dilute hydrochloric acid (1 to 1, prepared

TABLE I. ANALYSIS OF TITANIUM AND COLUMBIUM (PLUS TANTALUM) STAINLESS STEELS FOR NITROGEN

Type of Steel	Nitrogen		Composition of Steel								
	Acid soluble %	Acid insoluble %	Total N %	Cr %	Ni %	C %	Cb %	Ta %	Ti %	Mn %	Si %
18-8 + Cb	0.031	0.015	0.046	17.81	9.18	0.07	0.75	0.09	Not over 0.01	0.52	0.36
18-8 + Cb	0.15	0.07	0.21 0.22 <sup>a</sup>	18.18	8.80	0.062	1.10	0.04	..	..	..
18-8 + Ti	0.006	0.042	0.048	18.21	9.17	0.158	..	..	1.56	0.31	0.54
24 Cr + Ti	0.009	0.300	0.309 0.309 <sup>a</sup>	23.98	..	0.104	..	..	1.36	..	..
24 Cr + Ti	0.011	0.270	0.281	23.67	1.18	0.094	..	..	1.27	..	..

<sup>a</sup> Results obtained by vacuum fusion.

which consists in dissolving the sample in hydrochloric acid (sp. gr. 1.11), adding a strong solution of potassium hydroxide, distilling the ammonia over into a measured volume of standard sulfuric acid, and titrating the excess acid with standard alkali, is applicable to most stainless steels, provided they do not contain any metals such as titanium, columbium, niobium, tungsten, or vanadium, which form acid-insoluble residues. Tschischewski (5) stated that in a 0.35 per cent nitrogen and 0.84 per cent manganese steel he found a residue in hydrochloric acid that contained 0.000125 per cent of nitrogen. The authors have experienced no interference due to silicon, which undoubtedly is because of the use of hydrofluoric acid in the initial solution of the sample. However, the nitrogen in a titanium-treated steel, provided no titanium is added, will be found almost entirely in the hydrochloric acid-insoluble residue. If the steel is alloyed with columbium, tantalum, or vanadium, only part of the nitrogen will be in the insoluble residue. Since one or more of these elements are frequently present in stainless steels, it is not safe to omit testing any acid-insoluble residue for nitro-

gen by mixing ammonia-free water with hydrochloric acid, sp. gr. 1.19, from a fresh bottle that has just been opened, a little at a time, until the violent reaction ceases. Three milliliters of hydrofluoric acid (48 per cent, from a freshly opened bottle) are next added and the dish and its contents are heated on a hot-water bath until the solution of the alloy is practically complete. Should the alloy dissolve completely in the hydrochloric acid, the addition of hydrofluoric acid may be omitted and the solution of the alloy may be effected in a 150-ml. covered beaker.

While the alloy is being dissolved, 100 ml. of sodium hydroxide (500 grams per liter), several small pieces of mossy zinc, about 400 ml. of water, and 20 grams of tartaric acid are transferred to a 500-ml. Kjeldahl flask connected to a spray trap and a block-tin condenser. The apparatus used is shown in Figure 1. Two hundred milliliters of the solution are distilled over and discarded, and the alkaline solution in the Kjeldahl flask is then allowed to cool.

The solution of the alloy is removed from the hot-water bath, allowed to cool, and added to the sodium hydroxide solution in the Kjeldahl flask. The tartaric acid previously added to the alkaline solution serves to hold most of the iron and chromium in solution and thus makes the distillation much easier. The dish is rinsed successively with four 50-ml. portions of ammonia-free water. The contents of the flask are then boiled until 200 ml. of the distillate have passed over. The distillate is collected in 25 ml. or more of standard 0.02 N hydrochloric acid, depending upon



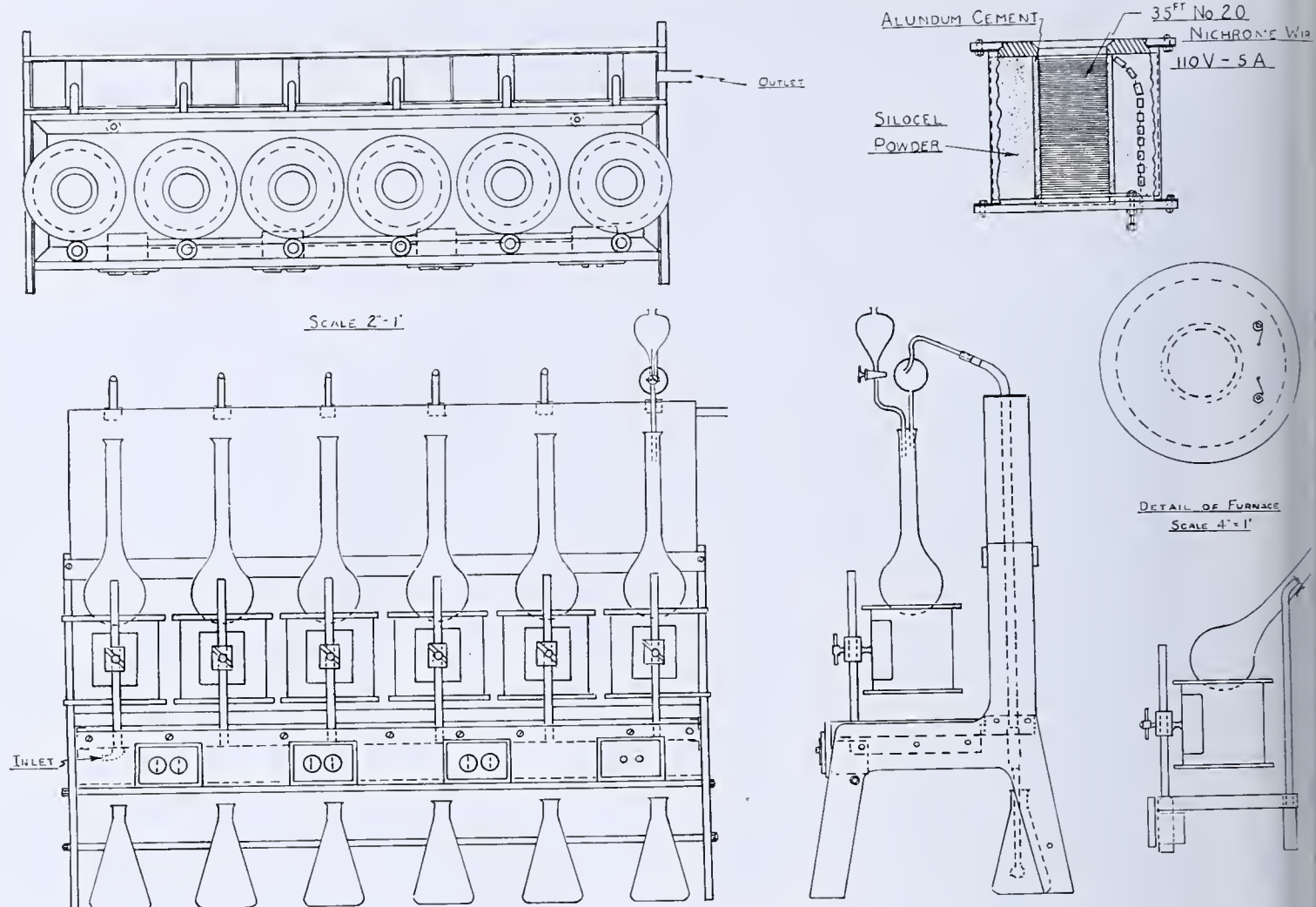


FIGURE 1. DIAGRAM OF APPARATUS

the nitrogen content of the alloy. The excess of acid is titrated with standard 0.02 *N* sodium hydroxide solution. Two drops of a 1 per cent aqueous solution of sodium alizarin sulfonate are used as an indicator. The end point is marked by the complete disappearance of the clear yellowish green color, or the first indication of a brown. Each milliliter of 0.02 *N* hydrochloric solution is equivalent to 0.00028 gram of nitrogen. A blank is run on all the reagents used and any nitrogen found is deducted. For steels containing very low percentages of nitrogen, solutions weaker than 0.02 *N* are used.

Should the steel contain vanadium, titanium, columbium, tantalum, or any other metals known to form a nitride insoluble in hydrochloric acid the solution obtained as described in the first paragraph should be filtered on a 9-cm. filter and the residue washed well with 1 per cent hydrochloric acid. The nitrogen in the filtrate is determined as described in paragraphs 2 and 3. The paper and insoluble residue are transferred to a 500-ml. Kjeldahl flask, 10 grams of potassium sulfate, 1 gram of copper sulfate, and 20 ml. of sulfuric acid (sp. gr. 1.84) are introduced, and the flask and its contents are heated just below the boiling point of the acid until all frothing ceases. At no time during the digestion should the part of the flask above the surface of the liquid be heated. The liquid is next heated to boiling and the boiling continued for from 15 to 30 minutes after the solution has become colorless. The solution is allowed to cool, 200 to 250 ml. of ammonia-free water are added, the flask is connected to the condenser, 150 ml. of 10-per cent sodium hydroxide solution are added, and the nitrogen in this solution is determined as described in paragraph 3. A blank is run on all the reagents used, including the filter paper, and any nitrogen so found is deducted. Any nitrogen found after deducting the "blank" is added to that obtained by acid solution of the sample and distillation, to obtain the total nitrogen.

Ammonia-free water is prepared by dissolving 200 grams of potassium hydroxide and 8 grams of potassium permanganate in 1100 ml. of distilled water and boiling the solution until the volume has been reduced to approximately 1000 ml. This solution is added to the water to be purified in the ratio of 1 to 10. Distillation is then carried on until a test of 100 ml. of the distillate does not require more than 1 or 2 drops of 0.02 *N* hydro-

chloric acid solution. Two drops of a 1 per cent aqueous solution of sodium alizarin sulfonate are used as the indicator.

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### Correction

In an article entitled, "A Modification of the Berl-Kulshammer Melting Point Block" [*IND. ENG. CHEM., Anal. Ed.*, 9, 34 (1937)] failure was inadvertently made to mention an article by Matthäus and Sauthoff [*Chem. Fabrik*, 8, 92 (1935)]. They have designed a block in which reflections from the sides of the melting point tube are eliminated by illumination from above. Unfortunately, this article was not abstracted in the American or British abstracts, upon which dependence was placed in the literature search (an abstract was later found in *Centralblatt*). The author wishes to acknowledge the priority of Matthäus and Sauthoff in regard to the feature of the block mentioned.

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April 24, 1939



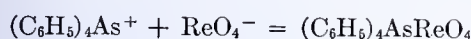
# Tetraphenylarsonium Chloride as an Analytical Reagent

## Determination of Rhenium

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THE perrhenate ion unites with the tetraphenylarsonium ion, in the reaction



form a white, crystalline precipitate which is insoluble in water. This permits the quantitative determination of rhenate both potentiometrically, by the titration of the excess reagent with iodine (1), and gravimetrically. The latter is usually more convenient and is the method described in this paper. The potentiometric titration is, however, equally satisfactory.

The determination is carried out by adding an excess of tetraphenylarsonium chloride to the perrhenate, keeping the volume as small as possible. The precipitate, which is allowed to stand several hours, preferably overnight, is filtered through a Gooch crucible, washed several times with water, dried, and weighed as  $(\text{C}_6\text{H}_5)_4\text{AsReO}_4$ . The precipitation is carried out in a hot solution, in the presence of a neutral salt, such as sodium chloride or sodium sulfate, to make the precipitate more granular and more easily transferred. The most satisfactory precipitation medium is 0.5 molar sodium chloride. Nitrates, except in very low concentration, should be avoided because of the limited solubility of tetraphenylarsonium nitrate.

TABLE I. GRAVIMETRIC DETERMINATION OF PERRHENATE  
(Volume, 25 to 60 ml.; NaCl, 0.5 molar)

Present Mg.	Perrhenate Found Mg.	Error Mg.
0.44	0.40	-0.04
0.89	0.91	+0.02
1.33	1.26	-0.07
1.78	1.82	+0.04
2.22	2.21	-0.01
4.44	4.43	-0.01
13.32	13.33	+0.01
17.76	17.82	+0.06
22.21	22.21	±0.00
22.21	22.17	-0.04
44.41	44.39	-0.02
88.82	89.00	+0.18
133.24	133.18	-0.06

Determinations were attempted in the presence of most of the common anions and cations. Anions, such as permanganate, periodate, perchlorate, thiocyanate, iodide, bromide, fluoride, which unite directly with the tetraphenylarsonium ion to form insoluble compounds, should be absent. For the cations the halide complexes of which form insoluble tetraphenylarsonium compounds in the presence of 0.5 molar chloride ions interfere except in very low concentrations. High concentrations, approaching saturation, of any substance should be avoided to prevent the precipitation of the excess reagent. In general, the presence of other substances in solution causes the formation of a precipitate which is more easily transferred.

### Procedure

In all determinations a standard solution, made by dissolving 0.8824 mg. of potassium perrhenate in water containing 8.824 mg. of perrhenate ion per ml. was used. To a definite volume of the solution, containing sufficient sodium chloride to make the

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final solution about 0.5 molar, a measured excess of tetraphenylarsonium chloride is added. The total volume should be 25 to 60 ml. The mixture is stirred and allowed to stand several hours, preferably overnight.

The precipitate is filtered through a Gooch crucible, washed several times with ice water, and dried at 110° C. It is weighed as tetraphenylarsonium perrhenate,  $(\text{C}_6\text{H}_5)_4\text{AsReO}_4$ . Multiplying by the factor 0.3952 converts this weight to perrhenate,  $\text{ReO}_4^-$ .

TABLE II. EFFECT OF ACIDITY AND ANIONS ON PERRHENATE DETERMINATIONS

(ReO <sub>4</sub> <sup>-</sup> , 22.21 mg.; total volume, 25 to 30 ml.)		
Substance Present	Molar Concentration	Perrhenate Error, Mg.
HCl	0.5	+0.04
HCl	4.8	+0.08
HNO <sub>3</sub>	0.7	+1.54
H <sub>2</sub> SO <sub>4</sub>	0.8	+0.09
H <sub>2</sub> SO <sub>4</sub>	3.6	+1.30
H <sub>3</sub> PO <sub>4</sub>	0.8	+0.07
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	6.9	+0.19
Citric acid	0.2	0.00
Tartaric acid	0.6	+0.08
Oxalic acid	0.3	+0.10
Na <sub>2</sub> SO <sub>4</sub>	0.5	-0.01
Na <sub>2</sub> WO <sub>4</sub>	0.1	+0.04
Na <sub>2</sub> HPO <sub>4</sub>	0.1	-0.11
NH <sub>4</sub> OH	6.0	+0.03
NaOH	0.5	-0.26

In this way quantities of perrhenate varying from 0.40 to 133 mg. have been determined with satisfactory accuracy in the presence of various other ions. Typical data are shown in Table I. Many of these gravimetric results were duplicated by the potentiometric titration of the excess of reagent with iodine.

TABLE III. EFFECT OF CATIONS ON DETERMINATION OF PERRHENATE (INCLUDING METAVANADATE, VO<sub>3</sub><sup>-</sup>)

(Volume, 25 to 35 ml.; NaCl, about 0.5 molar)				
Ion Present	Quantity of Ion Mg.	Perrhenate		Error Mg.
		Present Mg.	Found Mg.	
Al <sup>+++</sup>	112	22.21	22.13	-0.08
Ba <sup>++</sup>	565	44.41	44.34	-0.07
Ca <sup>++</sup>	360	44.41	44.34	-0.07
Cd <sup>++</sup>	440	22.21	22.17	-0.04
Co <sup>++</sup>	210	1.33	1.26	-0.07
Cr <sup>+++</sup>	215	44.41	44.50	+0.09
Cu <sup>++</sup>	255	44.41	44.34	-0.07
Fe <sup>++</sup>	200	2.22	2.29	+0.07
Fe <sup>+++</sup>	206	2.22	2.13	-0.09
Fe <sup>+++</sup>	206	44.41	44.34	-0.07
Mg <sup>++</sup>	100	22.21	22.21	0.00
Mn <sup>++</sup>	275	22.21	22.21	0.00
Ni <sup>++</sup>	250	22.21	22.13	-0.08
Sb <sup>+++</sup>	366	22.21	22.17	-0.04
UO <sub>2</sub> <sup>++</sup>	635	22.21	22.30	+0.09
VO <sup>++</sup>	200	44.41	45.01	+0.60
VO <sup>++</sup>	800	22.21	23.67	+1.46
VO <sup>++</sup>	1000	4.44	6.97	+2.53
VO <sub>3</sub> <sup>-</sup>	35	44.41	44.57	+0.16
VO <sub>3</sub> <sup>-</sup>	650	22.21	22.31	+0.10
VO <sub>3</sub> <sup>-</sup>	520	4.44	4.55	+0.11
Zn <sup>++</sup>	260	22.21	22.17	-0.04

Similar determinations were satisfactorily made under conditions of acidity varying from weakly alkaline to fairly strongly acidic. Sodium hydroxide has a solvent action on the precipitate, but a relatively high concentration of ammonium hydroxide is not harmful. Nitric acid or nitrates, except in very low concentration, will cause coprecipitation of tetraphenylarsonium nitrate with the perrhenate. High results are obtained with high concentrations of hydrochloric



acid or other acids, probably because of the decreased solubility of the reagent under such conditions. Bromide, iodide, and fluoride, in more than traces, should be absent. Tungstate does not interfere. Results are shown in Table II.

TABLE IV. EFFECT OF NITRATE AND MOLYBDATE ON PERRHENATE DETERMINATION

(Volume, 20 to 35 ml.; NaCl, about 0.5 molar)				
Substance Present	Concentration	Perrhenate		Error
		Present	Found	
		Mg.	Mg.	Mg.
NH <sub>4</sub> NO <sub>3</sub>	0.5 M	44.41	50.98	+6.57
NaNO <sub>3</sub>	0.3 M	22.21	25.77	+3.56
NaNO <sub>3</sub>	0.016 M	22.21	22.40	+0.19
NaNO <sub>3</sub>	0.1 M	0.89	0.91	+0.02
NaNO <sub>3</sub>	0.05 M	0.44	0.40	-0.04
	Mg. MoO <sub>3</sub>			
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	315	22.21	22.13	-0.08
MoO <sub>3</sub> + 3 g. tartaric acid	315	22.21	22.21	0.00
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	210	2.22	2.25	+0.03
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	210	44.41	44.34	-0.07
MoO <sub>3</sub> + 3 g. tartaric acid	210	44.41	44.26	-0.15
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	100	0.44	0.40	-0.04
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	100	2.22	2.21	-0.01
MoO <sub>3</sub> + 4 ml. NH <sub>4</sub> OH	100	22.21	22.29	+0.08
MoO <sub>3</sub> + 2 ml. NH <sub>4</sub> OH	20	22.21	22.17	-0.04
MoO <sub>3</sub>	100	22.21	120.26	+98.05

### Interfering Substances

The effect of the presence of various cations is shown in Table III. Only those ions interfere which form insoluble chlorides or whose complex halides form insoluble salts with tetraphenylarsonium ion. These include mercuric, stannic, bismuth, tellurium, lead, vanadyl, and silver. Cadmium and zinc do not interfere if the chloride-ion concentration is low. Metavanadate ion in fairly high concentration does not interfere. All these ions serve to make the precipitate more granular.

The presence of nitrate even in small quantities may cause serious interference if the quantity of perrhenate is fairly large. However, the interference is not so pronounced for very small amounts of perrhenate. It is practically impossible to wash out all traces of tetraphenylarsonium nitrate from the heavier perrhenate precipitate. Typical data are shown in Table IV.

Molybdate ion forms a fairly insoluble precipitate with tetraphenylarsonium ion, but this precipitation is hindered or prevented altogether in the presence of ammonium hydroxide, tartrates, citrates, and their acids. Typical data are shown in Table IV.

### Summary

From 0.40 to 133.0 mg. of perrhenate ion can be determined gravimetrically with tetraphenylarsonium ion, in moderate excess, in volumes from 25 to 60 ml.

The presence of a small amount of sodium chloride, about 0.5 molar, or of other salts, and heating before precipitation are very effective in producing a crystalline precipitate which is easily transferred and washed.

Accurate determinations may be made in solutions varying from strongly ammoniacal to fairly strongly acidic.

Permanganate, perchlorate, periodate, iodide, bromine, fluoride, thiocyanate, mercury, tin, vanadyl, and bismuth do not interfere.

Nitrate must be absent in all but very low concentrations. Interference by molybdate may be avoided by the use of ammonium hydroxide or tartaric acid.

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## Determination of Riboflavin in Milk

### By Photoelectric Fluorescence Measurements

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Riboflavin in milk was determined by adding 50 ml. of acetone to 25 ml. of milk, filtering, and comparing the fluorescence of the filtrate with that of a cube of uranium glass which had previously been calibrated against solutions containing known amounts of riboflavin. The comparison of fluorescence was made with a photoelectric cell and microammeter, using suitable glass filters.

**R**IBOFLAVIN or lactoflavin, the principal water-soluble pigment of milk and whey, is of interest because of its nutritional value as vitamin G (8), its behavior as a co-enzyme (15, 17), as a hydrogen acceptor (16), and as a photosensitizer for the oxidation of vitamin C in milk by light (5, 6, 12). The riboflavin content of milk can be determined rapidly and accurately by using suitable light filters and standards and measuring with a photoelectric cell and microammeter the fluorescence produced in a filtered acetone extract of milk or whey.

Methods for the determination of riboflavin so far described have involved visual estimation of color or fluorescence

intensity by comparison with standards, or photoelectric measurement of either light absorption or fluorescence intensity. Charite and Khaustov (1) compared riboflavin extracts with a standard solution of potassium chromate in a colorimeter. Kuhn, Wagner-Jauregg, and Kaltsech (11) determined the chloroform-soluble, photochemically composition product with a stage photometer. Koschar purified the riboflavin solutions with chromatographic sorption and oxidation by permanganate, and determined concentrations directly in a stage photometer. Sullivan measured the light absorption by the use of filters and a photoelectric cell. Euler and Adler (3) and later Supplee, Bacher, Flanagan, and Hanford (14) and Whitnah, Kunz, and Kramer (20) compared visually the fluorescence of known and standard riboflavin solutions. Weisberg and Levin (19) described a similar method but used fluorescent solutions as standards. Cohen (2) measured the intensity of fluorescence directly with a photoelectric cell and a filter, using fluorescein as a standard.

The methods based on light absorption have the advantage that the absorption coefficients reported are in absolute units and can be determined very accurately. However, many of the colored materials accompanying riboflavin interfere with the determination. Fluorescence measurements are



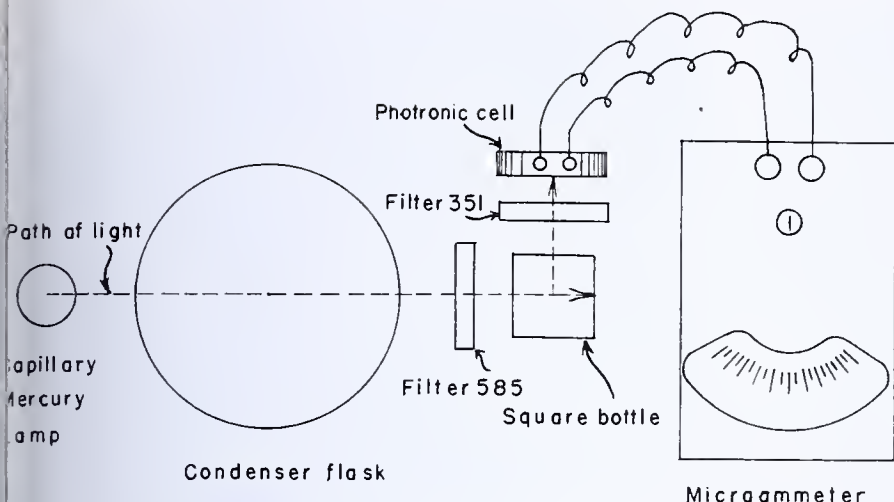


FIGURE 1. DIAGRAM OF FLUOROMETER

specific. Perhaps no other substance present in the acetone extract of the natural products yields a green fluorescence. Blue or violet fluorescence, sometimes observed, can be screened out by means of light filters. More important still, riboflavin occurs in milk in an amount convenient for fluorescence measurement but too small for ordinary direct colorimetric determination. The range for colorimetric determination is 4 to 40 mg. per liter, while the range for the fluorescence method is 0.1 to 4 mg. per liter.

### Construction of Apparatus

The author's apparatus consists of a photoelectric cell, a microammeter, a capillary mercury lamp, two glass filters, a cube of uranium glass, and a square glass bottle, arranged as shown diagrammatically in Figure 1, and mounted in a light-tight housing which definitely maintains the positions of the various parts. A liter Pyrex flask filled with distilled water serves as a condenser.

A sufficiently sensitive photronic cell can be obtained from Helz and Bauer, Empire State Bldg., New York, N. Y. The microammeter was full-scale 15s, 150 ohms internal resistance. The capillary mercury lamp was G. E. vertical type H-4, 100-watt, nonex envelope. The glass filters were from Corning, Y., 5 cm. (2 inches) square and unpolished, Nos. 585 and 351. The 25-mm. uranium glass cube was also from Corning. The square bottle was a 30-ml. dropping bottle, A. H. Thomas No. 18.]

The filters were selected to give maximum intensity of fluorescence and to absorb all stray light which might strike the photonic cell. The transmission of the first filter corresponds to the absorption of riboflavin between 3000 and 5000 Å.; the second filter absorbs nearly all the light in the range transmitted by the first filter, cutting the light off sharply below 5000 Å. Thus no blue or violet fluorescence can interfere and the effect of scattered light from slightly turbid solutions is minimized.

The separate units in the instrument were selected so as to provide sufficient fluorescence intensity for direct reading without the use of an amplifier and to minimize the destruction of riboflavin by light during the time of measurement. In the apparatus described here a 10 per cent destruction of riboflavin occurred in one minute, but since only 2 to 3 seconds are required for a reading, destruction of riboflavin during the determination is considered negligible. If the riboflavin is completely reduced or destroyed by light, readings on the instrument will fall to zero.

A slight fluctuation in the intensity of the light source is unavoidable. The lamp is operated by the 110-volt alternating current with the aid of a transformer and gives a remarkably steady light, much steadier than a tungsten lamp connected to the same line. To eliminate the error due to fluctuations in light intensity, readings for the unknown are compared immediately to readings produced by the fluorescence of a cube of uranium glass used as a working standard. From the ratio of these two readings the riboflavin concentration is calculated. It is impracticable to use riboflavin or fluorescein directly as standard solutions because both are destroyed by light. Riboflavin is used as an ultimate standard for comparison with the uranium glass and

the uranium glass is used as a working standard for comparison with the unknown solutions.

The uranium glass can be mounted conveniently in a square bottle identical with that used to hold the solutions to be tested. The bottle is first cut in two just below the shoulder. A piece of black paper containing a centered opening 1 cm. square should be pasted to the surface of the uranium glass facing the photonic cell. The base of the uranium glass is then imbedded in sealing wax and the bottle is cemented together. (The bottles are very easily cut after scratching all the way around, by touching each corner momentarily with a hot glass rod. The cracks are then led together by means of the hot rod. LePage's waterproof cement has proved useful in cementing the pieces together. The seal is permanent if kept dry.)

### Calibration

The fluorescence intensity of pure riboflavin was obtained by comparing the fluorescence of four purified riboflavin preparations with the standard uranium glass. (L. C. Norris kindly gave the author a sample of synthetic riboflavin supplied by R. Kuhn. Three commercial preparations of pure riboflavin were obtained from the Vitamin Products Company, Emoryville, Calif., and Borden Company, Bainbridge, N. Y.) These preparations were weighed in duplicate on a microbalance and stock solutions containing 0.1 mg. per ml. in 20 per cent alcohol were prepared and kept in the dark at 10° C. Table I gives the results. Since any deterioration of riboflavin would weaken its fluorescence, it is likely that the higher results with preparation 2 are more nearly correct. Moreover, preparation 2 was obtained more recently than the other three and was the only one of the four which dissolved without leaving a residue. A sample purchased a year later was found to be identical with the earlier sample. These stock solutions of riboflavin did not deteriorate in a year's time.

The fluorometer was calibrated by determining the variation of fluorescence intensity with concentration of riboflavin in a 66 per cent acetone filtrate from milk. For this calibration curve the stock solution of preparation 2 was added to an acetone filtrate from milk from which the riboflavin had been completely removed by exposure to sunlight. In this way the necessity of correcting for the riboflavin originally in the milk was avoided. Results are shown in Figure 2.

The absorption coefficients of riboflavin with various filter combinations were also measured as a further check on the purity of the preparations. As shown by Table I, the measurements of absorption coefficients agreed with the fluorescence measurements in indicating that the other preparations

TABLE I. COMPARISON OF RIBOFLAVIN PREPARATIONS

Preparation No.	Fluorescence <sup>a</sup> Intensity	Absorption Coefficient <sup>b</sup>	
		5 mg./liter	10 mg./liter
1	1.26	0.104	0.210
2	1.36	0.124	0.244
3	1.21	0.106	0.215
4	1.30	...	0.223
No. 2 in acetone - milk filtrate	1.20	...	...
Fluorescein	1.62	...	...

<sup>a</sup> Fluorescence intensity equals the ratio of stock solution readings to uranium glass readings with filters 585 and 351. The stock solutions (20 per cent alcohol) diluted to 1 mg. per liter in water. Fluorescein was Kahlbaum's, dissolved in 0.0011 N NaOH.

<sup>b</sup> Absorption coefficient equals  $\log_{10} \frac{I_0}{I}$  in water solution, tubes 1.0 cm. in internal diameter, 6-volt tungsten lamp, filters 585 + 556, photonic cell, microammeter of 150 ohms.



were less pure than preparation 2. Measurement of the absorption coefficient provides a valuable check on the purity of a riboflavin standard when it is necessary to recalibrate the apparatus—e. g., after replacing the mercury lamp. The molar extinction coefficient can be calculated from  $\log \frac{I_0}{I} = 0.0244$  for 1 mg. per liter by multiplying by  $364 \times 1000 \times 2.303$  and is found to be  $20.5 \times 10^3$ . This is in reasonable agreement with the value of  $24 \times 10^3$  at  $445 \text{ m}\mu$ , reported by

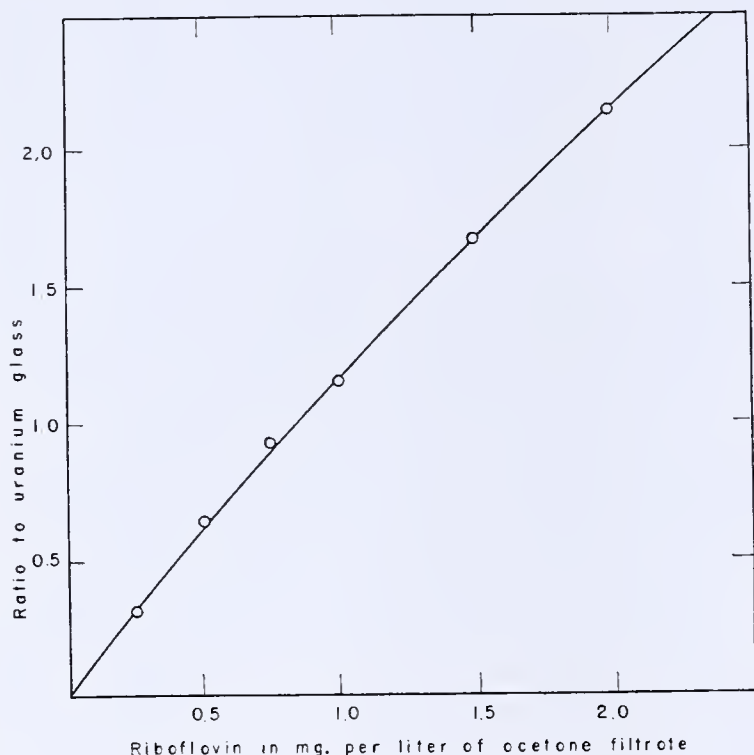


FIGURE 2. CALIBRATION OF FLUOROMETER  
For determining riboflavin in 66 per cent acetone filtrate from milk

Kuhn, György, and Wagner-Jauregg (9). A value approaching the maximum value for monochromatic light indicates that the riboflavin is pure and that the transmission of the filter and sensitivity of the photocell give a "band" corresponding closely to the absorption band of riboflavin between  $400$  and  $500 \text{ m}\mu$ .

Since the fluorescence of riboflavin depends on the nature of the solvent, it is necessary to calibrate the apparatus for each particular solvent. For example, the fluorescence of riboflavin is 13 per cent weaker in the 66 per cent acetone-milk filtrate than it is in pure water (Table I). Intensity decreases below pH 3 and above pH 9. The microammeter readings for fluorescence are nearly proportional to riboflavin concentration, as shown in Figure 2, in which the microammeter readings for riboflavin in 66 per cent acetone-milk filtrate divided by the microammeter reading for the uranium glass are plotted against concentration of riboflavin. The color of the fluorescence is almost but not exactly like that of uranium glass, as shown by the fact that the ratios are slightly different with different filters. There is a little more blue in the fluorescence of the uranium glass, but this difference is not visible in a pocket spectroscope.

### Procedure

Fifty milliliters of acetone were added to 25 ml. of whole milk and the mixture was filtered through a coarse 15-cm. filter. The first part of the filtrate was poured through the filter a second time. The clear filtrate was placed in the special bottle for measuring fluorescence and the ratio of its fluorescence to that of the standard uranium glass was determined. The concentration of

riboflavin in the filtrate was read from the calibration curve shown in Figure 2.

The results were calculated in milligrams per liter of whole milk, corrections being made for dilution by the acetone, the contraction on adding acetone to milk, and the volume of the fat and protein, as follows: When 50 ml. of acetone are added to 25 ml. of whole milk the total volume is 72.3 ml. The volume of the fat and protein which are precipitated from 25 ml. of whole milk by the acetone is calculated to be 1.6 ml., on the basis of 3 per cent by weight of casein and 3.5 per cent of fat. Therefore the riboflavin originally in 25 ml. of whole milk is diluted to 70.7 ml. acetone filtrate. The value for riboflavin in milligrams per liter of acetone filtrate is obtained directly from the ratio to uranium glass by reference to the calibration curve (Figure 2) and the value is multiplied by the dilution factor 2.83 to obtain the result in milligrams per liter of whole milk. The corresponding factors for skim milk is 2.87 and for whey 2.89. These factors can be used when the actual determinations are made on the material in which the concentration of riboflavin is to be calculated. Owing to removal by the casein the concentration of riboflavin actually present in whey is less than that calculated from a determination of riboflavin in whole or skim milk.

Practically the entire fluorescence of these clear solutions can be destroyed by irradiation or reduction. Less than 1 per cent of the fluorescence (through filter 351) is a bluish (or white) fluorescence or turbidity which is not destroyed by reduction or irradiation. Table II shows that riboflavin added to milk can be recovered quantitatively by this method. The milk in these experiments was first exposed to sunlight to cause the destruction of nearly all of the original riboflavin. Souring of the milk slows filtration, but has no measurable effect on the fluorescence. Pasteurizing, or holding for one week in the dark or for one hour in ordinary diffused room light, has no effect.

Variation of the normal riboflavin content of milk has been found to be from 1.20 to 3.40 mg. per liter in a series of 4 determinations. In view of the wide variation in individual milk samples, due to feed, breed, and especially to differences among individual cows in the same breed, the assignment of a normal value to the riboflavin content of milk would be misleading. The riboflavin content of milk can be best described in the form of a distribution curve which involves a large number of samples. Therefore to be of use in this connection a method should be designed for large numbers of determinations rather than for extreme accuracy.

The fluorometric method in addition to being extremely rapid is reliable to  $\pm 5$  per cent. The mean deviation for duplicate analyses on the same milk was found to be  $\pm 2$  per cent. While the accidental error is small, there is a chance of greater systematic error in impurities in the standard riboflavin, and in some change in the optical system of the apparatus.

TABLE II. RECOVERY OF ADDED RIBOFLAVIN  
(Showing that all the riboflavin in milk is extracted from the curd by 66 per cent acetone. Riboflavin values in mg. per liter)

Present in Original Milk (Determined)	Amount Added	Present in Milk after Addition (Calcd.)	Found by Analysis	Per Cent Error
Mg. per liter				
0.55		0.55	0.55	
0.55	0.25	0.80	0.81	+1.3
0.55	0.50	1.05	1.04	-0.9
0.55	0.75	1.30	1.32	+1.5
0.55	1.0	1.55	1.58	+1.9
0.55	1.5	2.05	1.91	-6.8
0.55	2.0	2.55	2.51	-1.6
0.55	3.13	3.68	3.81	+3.4

such as replacement of the light or alteration in the photocell. It is much simpler to get relative values for the different samples than to determine absolute quantities of riboflavin in milk. In order to get absolute values as accurately as possible, four riboflavin preparations have been examined and found to agree within 10 per cent (Table I). The fluorescence intensity of the best preparation is probably within



per cent of the fluorescence intensity of pure riboflavin. In order to make sure that the observed seasonal variations in fresh milk samples were real and not due to fluctuations in the standards, solutions of riboflavin and fluorescein have been kept for a year. Readings made at intervals throughout the year on these solutions have shown a mean deviation of  $\pm 5.0$  per cent from the mean values. This day-to-day fluctuation of the apparatus probably is the limiting factor in the accuracy of the fluorometric method when uranium glass is used as a standard over long periods of time. However, the fluctuation can be eliminated by comparing the uranium glass with a fresh stock solution of riboflavin each time a determination is made. In this way the error of comparative readings can be reduced to  $\pm 2.2$  per cent, which is the mean deviation from the mean for duplicate analyses. But much of the convenience of the method is sacrificed and the accuracy of the absolute values of riboflavin is still limited by the purity and reproducibility of the standard riboflavin preparations.

The method gives the value for the total riboflavin regardless of whether it is free or combined with protein. Preparations of the combined form of riboflavin (yellow enzyme) have been made from yeast according to the directions of Warburg and Christian (18). Analyses of this material yielded the same results by precipitation with acetone as by refluxing 10 minutes in 75 per cent methyl alcohol with or without 0.2 per cent glacial acetic acid. Precipitation by acetone yields higher readings and less turbid solutions than precipitation by trichloroacetic acid. Apparently 66 per cent acetone at room temperature is sufficient to separate the riboflavin from the protein, presumably by denaturing and precipitating the protein. Moreover, Kuhn and Kaltschmitt (10) state that riboflavin in milk occurs in the free

form. Since they succeeded in removing 90 per cent by water dialysis there is no convincing evidence that any bound flavin occurs in milk (4, 10). Because of its accuracy, rapidity, and specificity the fluorometric method is perhaps more suitable than either the biological method or the colorimetric method for determining riboflavin in milk.

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## Determination of Nickel and Cobalt in Silicate Rocks

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THE method here described for the determination of nickel is based on the extraction of nickel dimethylglyoxime from chloroform from the ammoniacal citrate solution of the rock sample. By shaking the chloroform extract with dilute hydrochloric acid the dimethylglyoxime compound is decomposed and nickel is brought into the aqueous phase, in which it is then determined colorimetrically by Rollet's method (3). This method is particularly designed for rocks of such low nickel content that the nickel cannot well be determined by the gravimetric method of Harwood and Theobald (2).

### Procedure

Weigh 0.25 gram of finely powdered basic rock (0.01 to 0.05 per cent nickel), or 0.5 gram or more of acidic rock, into a platinum dish, add a few milliliters of water, 0.5 ml. of 70 per cent perchloric acid, and 2.5 ml. of hydrofluoric acid (for a sample greater than 0.5 gram these amounts should be correspondingly increased). Evaporate the mixture to dryness, take up the residue in 0.5 ml. of perchloric acid and 2 or 3 ml. of water, and again evaporate to dryness. To the residue add 0.5 to 1 ml. of concentrated hydrochloric acid and 5 ml. of water. Heat to bring all soluble material into solution, add 5 ml. of 10 per cent sodium citrate solution, neutralize the cold solution with concentrated ammonium hydroxide using litmus paper, and add a few drops in excess. If there is an appreciable amount of precipitate or residue in the

solution at this point, filter through a small paper, wash with small portions of water, and ignite the paper and its contents. Fuse the residue with approximately 0.1 gram of sodium carbonate, add an excess of dilute hydrochloric acid to the cooled melt, and heat to effect as complete solution as possible. Add 2 or 3 ml. of 10 per cent sodium citrate solution, make slightly ammoniacal, and reserve the solution.

To the main solution (filtrate from any insoluble material) add 2 ml. of 1 per cent alcoholic dimethylglyoxime solution, and shake vigorously for one-half minute with two or three portions of reagent-quality chloroform, each having a volume of 2 or 3 ml. In a similar manner extract the ammoniacal solution of the sodium carbonate melt. Combine all the chloroform extracts and shake vigorously with 10 ml. of 1 to 50 ammonium hydroxide solution. Draw off the chloroform, taking care that no drops of the aqueous phase accompany it, and shake the water layer with a milliliter or two of chloroform to recover any suspended drops of chloroform solution.

Shake the chloroform solution of nickel dimethylglyoxime vigorously for 1 minute with two portions of 0.5 N hydrochloric acid, each having a volume of 5 ml. (or slightly less if the solution is finally to be made up to 10 ml.). Transfer the hydrochloric acid solutions to a volumetric flask of suitable size or a flat-bottomed color comparison tube (1.8  $\times$  15 cm.), taking care that no appreciable amount of chloroform is carried over. For color comparison in a colorimeter the nickel concentration of the final solution should be at least 1 microgram per ml. For most acidic rocks the standard series method of color comparison will



usually have to be applied because of the low nickel content. A suitable series of standards for a silicic rock is 0, 1, 2, . . . . 10 micrograms of nickel for a 0.5-gram sample. Whether a colorimeter or tubes are used, the final nickel concentration should not exceed 5 micrograms per ml. or else a precipitate of nickel dimethylglyoxime may be produced.

The unknown nickel solution and the standard nickel solution diluted to about 10 ml. with 0.5 *N* hydrochloric acid are treated simultaneously as follows: Add 5 drops of freshly prepared saturated bromine water, mix, and then add concentrated ammonium hydroxide dropwise with shaking until the color of bromine disappears; finally add an excess of 3 or 4 drops. Next add 0.5 ml. of 1 per cent alcoholic dimethylglyoxime solution, mix, and dilute to volume with water if a volumetric flask is used. The color comparison may be made immediately. The color intensity of the solutions increases slowly on standing; the unknown and standard solution should therefore be treated with the reagents at the same time.

If necessary apply a correction for nickel in the reagents.

TABLE I. DETERMINATION OF NICKEL

No.	Sample	Addition	Ni Taken <sup>a</sup> %	Ni Found %	Error %
1	Extracted <sup>b</sup> solution of granite	.....	0.0003	0.0003	0.0000
2	Synthetic basic rock	.....	0.0020	0.0018	-0.0002
3	Extracted solution of synthetic basic rock	.....	0.0020	0.0019	-0.0001
4	Synthetic basic rock	.....	0.0060	0.0060	0.0000
5	Synthetic basic rock	.....	0.011	0.011	0.000
6	Synthetic basic rock	.....	0.021	0.020	-0.001
7	Synthetic basic rock	.....	0.042	0.041	-0.001
8	Synthetic basic rock	0.04% Co	0.0030	0.0028	-0.0002
9	Synthetic basic rock	0.03% Cu	0.010	0.010	0.000
10	Synthetic basic rock	0.1% Cu, 0.05% Co	0.009	0.010	+0.001
11	Synthetic basic rock	1.0% Mn	0.011	0.011	0.000
12	Synthetic basic rock	0.2% Cr <sup>VI</sup> , 0.05% V <sup>V</sup>	0.020	0.020	0.000

<sup>a</sup> Includes nickel originally present in synthetic basic rock (0.0010%). For composition of synthetic basic rock see (4).  
<sup>b</sup> Solution of sample extracted with chloroform after addition of dimethylglyoxime to remove nickel originally present, and nickel then added to extracted solution.

Discussion

The results obtained by applying the foregoing directions are given in Table I. One-fourth gram samples were used and the color comparison was made in a Duboscq colorimeter when the nickel content was 0.005 per cent or greater. The sensitivity of the method is great enough to allow the detection of less than 0.0001 per cent of nickel when a 0.5-gram sample is taken.

Copper, cobalt, manganese, chromium, and vanadium in the amounts that are likely to be encountered in most igneous rocks do not interfere. It may be expected that much copper and cobalt will lead to high results. One hundred micrograms of cobalt carried through the procedure gave a color corresponding to about 1.5 micrograms of nickel, and 100 micrograms of copper gave no color. Manganese in large quantities may cause trouble by oxidizing nickel to the nickelic condition in the ammoniacal solution during shaking, and the results for nickel will then be low, because nickelic dimethylglyoxime is not extracted by chloroform.

Under the conditions specified above for the final determination of nickel, Beer's law is closely followed up to a concentration of about 6 micrograms of nickel per milliliter. Above this concentration a precipitate may separate.

The solubility of nickel dimethylglyoxime in chloroform at room temperature corresponds to approximately 50 micrograms of nickel per milliliter.

Cobalt

The following method for the determination of cobalt in silicate rocks is based on the extraction of the element with a carbon tetrachloride solution of dithizone from the ammoni-

acal citrate solution of the sample. The carbon tetrachloride extract, which also contains the dithizonates of copper and other heavy metals, is evaporated to dryness, the residue is ignited to destroy organic matter, and the metal oxides are dissolved in aqua regia. The solution is treated with stannous chloride to reduce copper to the cuprous condition, and cobalt is then determined colorimetrically by the addition of ammonium thiocyanate and acetone, essentially according to the directions of Tomula (5). Nickel accompanies cobalt to a greater or less extent in the dithizone separation, but because of the low concentration it usually does not markedly affect the determination of cobalt even when the ratio of nickel to cobalt in the final solution is 10 to 1. Alternatively, cobalt can be determined by the thiocyanate-amyl alcohol method (1) in which large amounts of nickel do not interfere. By using a 1-gram sample, 0.0001 per cent of cobalt can be detected by either method.

Tables II and III contain some of the results obtained in applying the procedure described below.

PROCEDURE. Decompose 0.25 gram of basic rock, or 0.5 to 1 gram of acidic rock, as described above, making a sodium carbonate fusion of any insoluble material.

To the main solution (filtrate from any insoluble material after the hydrofluoric acid decomposition), containing 5 ml. of 10 per cent sodium citrate and at least 0.2 to 0.25 ml. of concentrated ammonium hydroxide in excess (these quantities are for a 0.25-gram sample), add 5 ml. of 0.01 per cent (weight by volume) dithizone in carbon tetrachloride. Shake vigorously for one-half minute and draw off the carbon tetrachloride extract. Add 2 or 3 ml. of dithizone to the solution, shake as before, and continue in this manner until the last portion of dithizone does not become red after shaking for 1 minute. In like manner extract the ammoniacal citrate solution of the sodium carbonate melt with a milliliter or two of dithizone. Wash the combined carbon tetrachloride extracts with 5 ml. of water, and run the carbon tetrachloride layer into a small silica dish, being careful to avoid the transfer of any aqueous phase.

Evaporate the carbon tetrachloride, rinse the upper portion of the dish with a few drops of carbon tetrachloride to wash down any residue, and ignite at redness to destroy organic matter. Care must be taken to burn off all organic material, but too prolonged heating or too high a temperature should be avoided. Add 2 or 3 drops each of hydrochloric and nitric acids, distribute

TABLE II. DETERMINATION OF COBALT BY THIOCYANATE-ACETONE METHOD

No.	Sample <sup>a</sup>	Addition	Co Taken <sup>b</sup> %	Co Found %	Error %
1	Synthetic basic rock	.....	0.0012	0.0010	-0.0002
2	Synthetic basic rock	.....	0.0048	0.0048	0.0000
3	Synthetic basic rock	.....	0.0100	0.0100	0.0000
4	Synthetic basic rock	.....	0.0250	0.0235	-0.0015
5	Synthetic basic rock	0.05% Ni	0.0048	0.0045	-0.0003
6	Extracted solution of synthetic basic rock	0.02% Cu	0.0048	0.0048	0.0000
7	Synthetic acid rock	.....	0.0004	0.0004	0.0000
8	Synthetic acid rock	.....	0.0009	0.0008	-0.0001
9	Extracted solution of synthetic acid rock	0.03% Ni	0.0003	0.0003	0.0000

<sup>a</sup> 0.25 gram of synthetic basic rock, 1.0 gram of synthetic acid rock.  
<sup>b</sup> Includes Co present in synthetic rock samples (0.0002% in basic rock, 0.0001% in acid rock).

TABLE III. DETERMINATION OF COBALT BY THIOCYANATE-AMYL ALCOHOL METHOD

No.	Sample <sup>a</sup>	Addition	Co Taken %	Co Found %	Error %
1	Synthetic acid rock	....	0.0003	0.0002	-0.0001
2	Extracted solution of synthetic acid rock	.....	0.0005	0.0005	0.0000
3	Synthetic acid rock	0.03% Ni	0.0001	0.0001	0.0000
4	Extracted solution of synthetic acid rock	0.02% Ni	0.0005	0.0005	0.0000
5	Synthetic acid rock	0.03% Cu	0.0004	0.0003	-0.0001
6	Synthetic acid rock	0.05% Ni, 0.01% Cu	0.0006	0.0006	0.0000
7	Granite	....	0.00075 <sup>b</sup>	0.0007	-0.00005

<sup>a</sup> 1.0-gram sample.  
<sup>b</sup> 0.00025% Co present in sample, 0.0005% Co added.



the liquid over the interior of the dish with the aid of a stirring rod, and evaporate to dryness on the steam bath. Add to the old dish 0.5 ml. of water and 3 or 4 drops of stannous chloride solution (20 grams of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 100 ml. of 2 *N* hydrochloric acid). Transfer the solution to a small glass-stoppered flat-bottomed tube (1 × 8 cm.) or a small vial. (A colorimeter may be used for the color comparison when the cobalt concentration is greater than 2 micrograms per milliliter of final solution.) Rinse the dish with 0.5 ml. of ammonium thiocyanate (50 grams in 100 ml. of water), then with 2 ml. of reagent-quality acetone, and transfer these washings to the tube. The concentration of acetone in the final solution must be at least 50 per cent by volume. After mixing, make the color comparison against a series of standards containing the same amounts of stannous chloride, ammonium thiocyanate, and acetone as the unknown. The percentage of cobalt in a basic rock such as a gabbro or diabase is likely to be less than 0.01 and the standards can be prepared accordingly. In acidic rocks the percentage is likely to be less than 0.001. The color of the sample solution should be pure blue, differing little if at all in hue from the standards. A greenish hue may be due to incomplete destruction of organic matter,

insufficient stannous chloride to reduce copper, or the presence of much nickel.

Alternatively the cobalt determination can be made by the amyl alcohol extraction method. This method should be used when much nickel is present in the sample, and it is also recommended for acidic rocks. Transfer the cobalt solution, treated with stannous chloride as before, to a 1 × 8 cm. glass-stoppered tube, and add 1.5 ml. of ammonium thiocyanate solution (50 grams in 100 ml. of water) and 0.50 ml. of amyl alcohol. Treat the standards similarly. Shake vigorously for 10 to 15 seconds and compare the colors of the amyl alcohol layers by viewing the tubes transversely against a white background.

Run a blank on the reagents and apply a correction if required.

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## Control of pH in Peroxide Solutions

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Control of pH is important in processes involving the production and applications of the peroxygen compounds. The applicability of colorimetric and potentiometric methods for measuring the pH of peroxide solutions is discussed and data are presented showing relationships between pH and normality of hydrogen peroxide solutions in concentrations up to 200 volume. Hydrogen peroxide behaves like a weak acid and increases the hydrogen-ion activity of sulfuric acid in proportion to the peroxide concentration.

PEROXYGEN compounds vary in their behavior with the pH of the solutions in which they are employed. The methods available for measuring and controlling the pH of oxidizing solutions are contributing markedly to the development of the chemistry of peroxygen compounds and to the extension of their commercial applications. In processes employing sodium peroxide, hydrogen peroxide, or sodium perborate, pH control has become fully as important as control of temperature, time, and concentration.

The pH of peroxide solutions has an important bearing on their stability. Peroxides are most stable in acid solutions and their rate of decomposition increases with the hydroxyl-ion concentration. Stability is furthermore influenced by inhibitors and catalysts whose activity depends upon the pH of the peroxide solution.

Rate and degree of bleaching with peroxides depend largely on the pH maintained in the particular bleaching processes. The catalytic effect of peroxides on hydrolytic reactions may be inhibited or accelerated by pH control. Rates of corrosion of structural materials are affected by changes in pH. In general, the desired properties of the peroxygen compounds can be promoted and their undesirable reactions can be suppressed by proper pH control.

### Methods for pH Determination

Some of the colorimetric indicators are affected by oxidizing compounds. However, with a proper choice of indicators, colorimetric methods can be satisfactorily applied in many cases. Among the electrode systems, the hydrogen gas electrode, the quinhydrone electrode, and the metal-metal ion electrode, such as the antimony electrode, are subject to large errors in the presence of oxidizing agents (6). The glass electrode, one of the more recent developments in pH measurement, is well adapted to potentiometric pH measurements in oxidizing and reducing systems, and is suitable for determining the pH of peroxide solutions. It has the advantage over colorimetric methods that it can be employed successfully in highly colored or turbid solutions.

The pH values presented in this article have been corrected for sodium-ion concentration in accordance with instructions supplied by the manufacturer of the pH meter. These corrections correspond closely with those given by Dole (4). No corrections were made at pH values below 9.3; the maximum correction of 0.4 pH unit was applied at the highest pH value shown—i. e., to the solution containing no hydrogen peroxide at a pH of 12.3.

### Comparison of Colorimetric and Potentiometric Methods

Figure 1 shows the agreement between colorimetric and glass electrode pH determinations for clear, colorless hydrogen peroxide solutions varying in concentration from 0 to 200 volumes. [A commonly used term for expressing the active oxygen content of peroxide solutions is "volume concentration", which is defined as the number of cubic centimeters of oxygen gas, measured at 0° C. and 760-mm. pressure, liberated from 1 cc. of the solution (measured at 20° C.) when the peroxide is completely decomposed.] The potentiometric determinations were made with a Beckman pH meter which provides for temperature corrections. The colorimetric determinations were made at a temperature of 20° to 30° C.; in this range variations in pH with changes in temperature



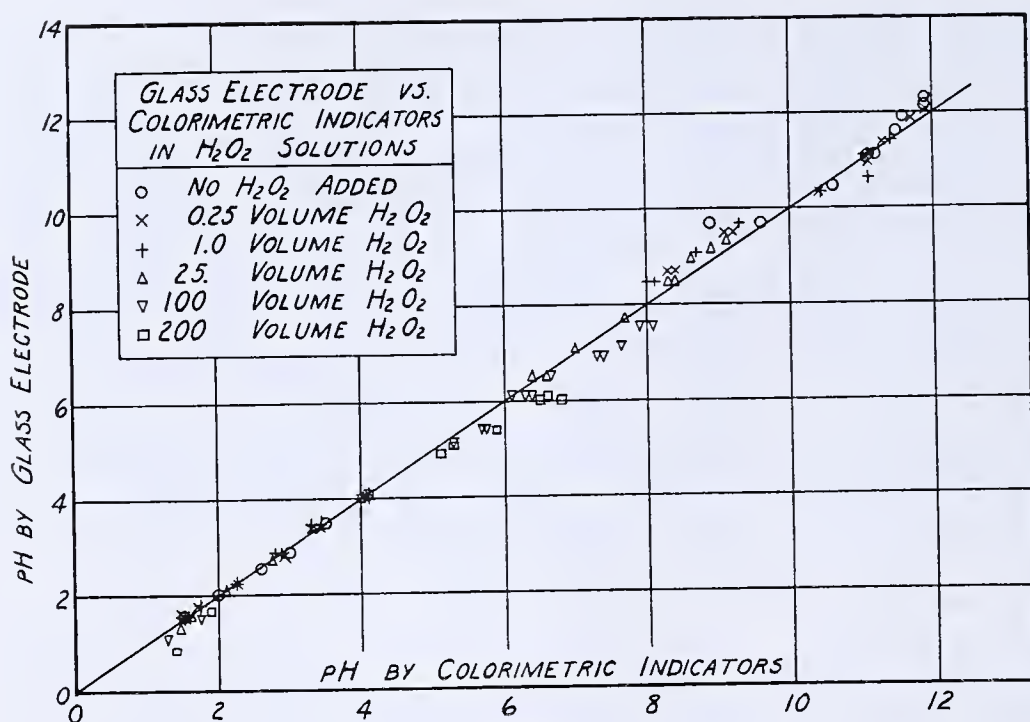


FIGURE 1

are negligible. The following La Motte colorimetric indicators were employed:

Indicator	pH Range
<i>m</i> -Cresol purple	1.2-2.8
La Motte yellow	2.6-4.2
Bromophenol blue	3.0-4.6
Bromocresol green	3.8-5.4
Chlorophenol red	5.2-6.8
Bromocresol purple	5.2-6.8
Bromothymol blue	6.0-7.6
Phenol red	6.8-8.4
Cresol red	7.2-8.8
Thymol blue	8.0-9.6
La Motte oleo red	8.6-10.2
La Motte purple	9.6-11.2
La Motte sulfo orange	11.0-12.6

In general, the values obtained by the two methods are in fair agreement, though in some cases the variation is as much as 0.8 pH unit. The closest agreement was obtained in the acid range with *m*-cresol purple, La Motte yellow, bromophenol blue, and bromocresol green. With these indicators the maximum difference between observed colorimetric and potentiometric pH values was less than 0.2 pH unit at peroxide concentrations up to and including 100 volume. In concentrations up to one volume the pH values obtained with La Motte sulfo orange also coincided within 0.2 pH unit with the potentiometric values. With the remaining indicators, the colorimetric pH values coincided in most cases within 0.4 pH unit with the potentiometric values. With some indicators differences in color tone made color matching between the standards and the unknown difficult.

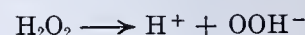
### Relation between pH and Normality

The pH curves shown in Figure 2 are derived from the data presented in Tables I and II. Each value in these tables is based on a separately prepared solution. The requisite amounts of hydrogen peroxide solution and standard sodium hydroxide or sulfuric acid solution were diluted in volumetric flasks, from which the samples were then removed for pH measurement. In this way errors due to dilution of the peroxide and of the acid or alkali were avoided.

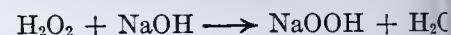
A number of pH measurements were made on 100-volume solutions containing the usual small amount of inorganic salts and on 100-volume solutions freed from these salts by redistillation. Comparisons were made at and near the vertical

and most sensitive section of the curve. The two sets of values coincided closely, indicating that no appreciable change in the location of the curves resulted from the use of redistilled peroxide.

The curves obtained illustrate the weakly acid property of hydrogen peroxide as reported by Bredig and Calvert (1, 2). In the alkaline range the pH decreases with increase in peroxide concentration at a fixed sodium hydroxide concentration. Assuming that hydrogen peroxide in aqueous solution undergoes primary dissociation according to the equation



it should react with caustic soda according to the equation



In Figure 2 the neutralization of the hydrogen ions resulting from the primary dissociation of hydrogen peroxide is theoretically complete in 0.25-volume hydrogen peroxide with 0.0223 *N* sodium hydroxide. A slight break, similar to the breaks encountered in the titration of a weak acid with strong base, might be expected at this point in the curve; however, no such break is apparent. With the higher concentrations of hydrogen peroxide (1.0, 25, 100, and 200

TABLE I. RELATION BETWEEN pH AND NORMALITY

H <sub>2</sub> O <sub>2</sub> Volume Concentration	H <sub>2</sub> SO <sub>4</sub> Normality	pH Glass Electrode
0.0	0.0001	4.12
0.0	0.0004	3.49
0.0	0.0016	2.90
0.0	0.0064	2.28
0.0	0.0128	2.02
0.0	0.0512	1.55
0.25	0.0001	4.07
0.25	0.0004	3.40
0.25	0.0016	2.82
0.25	0.0064	2.24
0.25	0.0256	1.78
0.25	0.0512	1.55
1.0	0.0001	4.10
1.0	0.0004	3.46
1.0	0.0016	2.88
1.0	0.0064	2.28
1.0	0.0256	1.80
1.0	0.0512	1.55
25	0.0001	4.08
25	0.0004	3.40
25	0.0016	2.75
25	0.0064	2.12
25	0.0256	1.60
25	0.0512	1.35
100	0.0004	3.05
100	0.0064	1.55
100	0.0256	1.00
100	0.0512	0.80
200	0.0004	2.80
200	0.0016	1.63
200	0.0064	0.85
200	0.0256	0.20
200	0.0512	0.00

volume) the highest concentration of sodium hydroxide used (0.05 *N*) is too low to neutralize completely the first hydrogen ion; consequently, no breaks are to be expected in the curves for these concentrations of hydrogen peroxide within the normalities presented. In an exploratory trial with 100-volume hydrogen peroxide the concentration of sodium hydroxide was increased to extend the curve in Figure 2 beyond



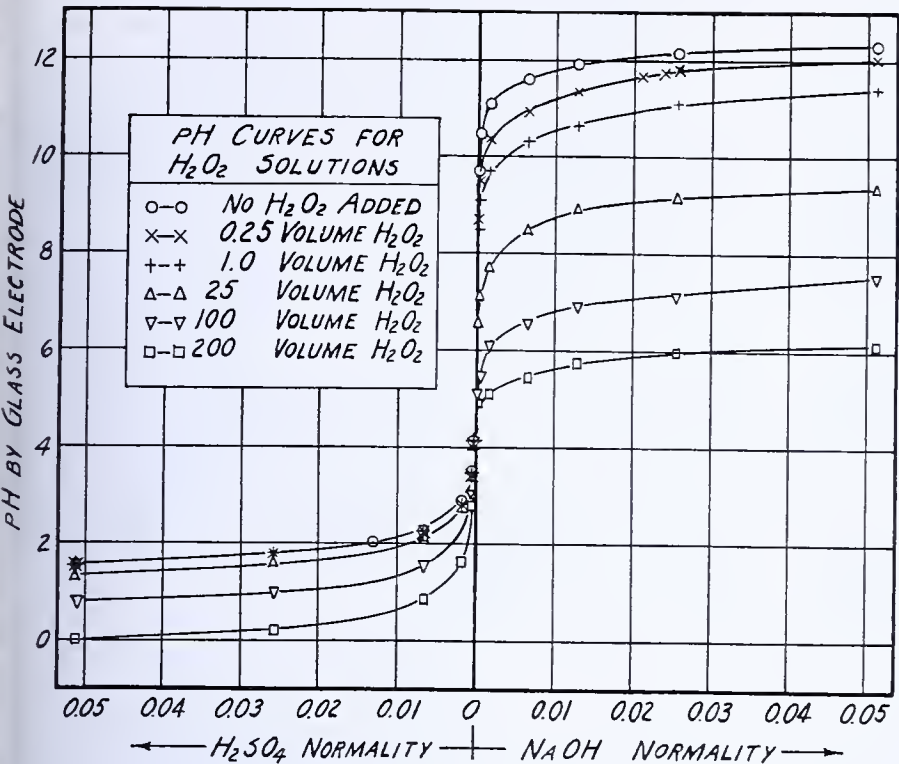


FIGURE 2

the point of neutralization (89 grams of sodium hydroxide per liter). A slight break was apparent in the curve at the point of equivalence. However, potentiometric pH measurements at these high sodium-ion concentrations are subject to considerable error and the slight break observed at this point in the curve may not be significant.

In the acid range of the curves the pH of the solution is abnormally lowered as the peroxide concentration is in-

creased. With complete dissociation and an activity coefficient of 1, the calculated pH is 1.3 at an acid concentration of 0.05 N. A 200-volume hydrogen peroxide solution showed a measured pH of 0.0 at a sulfuric acid concentration of 0.05 N. A dissociation constant of  $2.4 \times 10^{-12}$  for hydrogen peroxide at 25° C., as determined by Joyner (5), is not sufficient to account for this lowering in the observed pH value.

The dielectric constants for hydrogen peroxide solutions are considerably greater than the dielectric constant for water (3). Hence, the ionizing power of peroxide solutions should be greater than that of water, and this might be expected to result in an increased hydrogen-ion activity. Cuthbertson and Maass (3) did not find this to be the case in their studies of the conductivity of potassium chloride and acetic acid in aqueous hydrogen peroxide solutions. The authors' present data, however, show an increased hydrogen-ion activity for sulfuric acid dissolved in aqueous solutions of hydrogen peroxide.

At a constant concentration of sulfuric acid the observed pH values decrease as the peroxide concentration increases. This di-

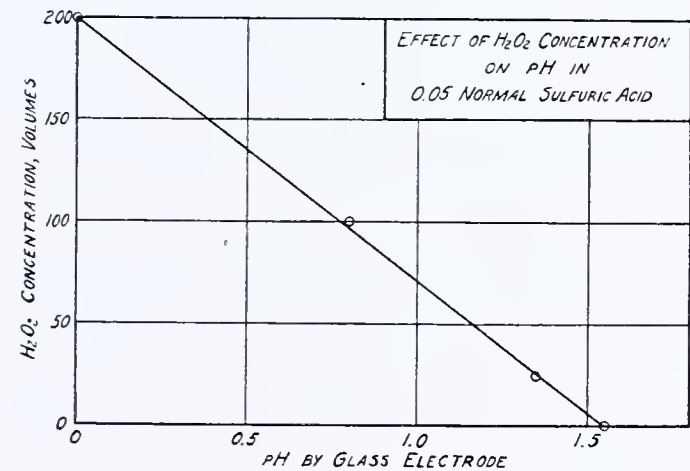


FIGURE 3

rect relationship is illustrated by the straight line shown in Figure 3, which represents the variation of pH with increasing peroxide concentration at a constant sulfuric acid concentration of 0.05 N. A similar curve illustrating the conditions at 0.025 N sulfuric acid produces a straight line with the same slope as that in Figure 3. This relationship, as derived from Figure 3, is represented by the equation

$$pH_{H_2O_2} = pH_{H_2O} - K \text{ (concentration of } H_2O_2)$$

where  $pH_{H_2O_2}$  is the pH of a sulfuric acid solution in aqueous hydrogen peroxide,  $pH_{H_2O}$  is the measured pH of an aqueous solution of the same sulfuric acid concentration, and  $K$  is a constant. If the strength of the peroxide solution is expressed as volume concentration, the value of 0.008 is found to apply for  $K$  at acid concentrations of 0.015 to 0.05 N. The value for  $K$  decreases slightly with decreasing acid concentrations; it is 0.0072 at 0.0064 N sulfuric acid and 0.0064 at 0.0016 N acid.

Summary

Determination and control of pH are important factors in processes employing peroxygen compounds, such as sodium peroxide, hydrogen peroxide, and sodium perborate.

TABLE II. RELATION BETWEEN pH AND NORMALITY

H <sub>2</sub> O <sub>2</sub> Volume Concentration	NaOH Normality	pH Glass Electrode
0.0	0.0001	9.70
0.0	0.0004	10.44
0.0	0.0016	11.07
0.0	0.0064	11.59
0.0	0.0128	11.91
0.0	0.0256	12.16
0.0	0.0512	12.29
0.25	0.0001	8.70
0.25	0.0004	9.50
0.25	0.0016	10.35
0.25	0.0064	10.94
0.25	0.0128	11.35
0.25	0.0210	11.64
0.25	0.0240	11.73
0.25	0.0256	11.82
0.25	0.0512	12.02
1.0	0.0001	8.47
1.0	0.0004	9.08
1.0	0.0016	9.69
1.0	0.0064	10.32
1.0	0.0128	10.62
1.0	0.0256	11.08
1.0	0.0512	11.40
25	0.0001	6.55
25	0.0004	7.08
25	0.0016	7.70
25	0.0064	8.45
25	0.0128	8.93
25	0.0256	9.15
25	0.0512	9.37
100	0.0001	5.13
100	0.0004	5.43
100	0.0016	6.10
100	0.0064	6.55
100	0.0128	6.93
100	0.0256	7.14
100	0.0512	7.52
200	0.0004	4.90
200	0.0016	5.07
200	0.0064	5.40
200	0.0128	5.75
200	0.0256	5.98
200	0.0512	6.10



The relationships between pH values, normalities, and peroxide concentrations, as presented in this article, are useful in the preparation of peroxide solutions with the desired pH values.

The glass electrode provides a simple method for rapidly and accurately determining the pH of peroxide solutions. This method is applicable to colored or turbid solutions, but in solutions of high pH and high sodium-ion concentration, corrections are necessary.

Colorimetric methods are applicable for determining the pH of peroxide solutions under many conditions, particularly in clear and colorless solutions.

In hydrogen peroxide solutions containing sulfuric acid

the hydrogen-ion activity increases with the peroxide concentration.

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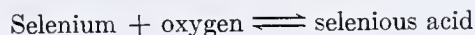
# Estimation of Nitrogen by the Kjeldahl Method

## Nature of the Action of Selenium

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FOLLOWING Lauro's (6) observation that selenium in small quantities reduces the time of digestion in the usual Kjeldahl method, numerous workers (1, 3, 9, 10) have studied the problem. Thus, considerable advance has been made in our knowledge of the optimum conditions of digestion when selenium is added. Beet and Furzey (2) reported that addition of small amounts of mercuric oxide (0.5 gram) along with 0.05 gram of selenium reduces the period of digestion to approximately 15 minutes as against 45 minutes required for complete digestion when only selenium is added to the usual acid and salt mixture.

Attempts were made to find out the exact mechanism and nature of the action of selenium, when added alone and with mercuric oxide. Snider and Coleman (11) thought that the function of selenium might be due to the elevation of the boiling point of the salt-acid mixture, but their experiments showed that it was not so. Recently, Illarionov and Ssolovjeva (5), in trying to explain the loss of nitrogen when selenium is used in the usual Kjeldahl method, suggested the occurrence of an oxidation-reduction system of the type



but they adduced no experimental evidence in support of their view. Therefore, the changes in the added selenium were studied in order to find out the mechanism of the reaction.

### Experimental

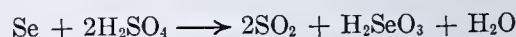
Selenium was used in the authors' experiments as either elementary selenium or its acids. It was found convenient to use the copper salts, since selenic acid is reduced under ordinary conditions to selenious acid.

The copper salt of selenic acid was prepared as described by Huff and McCrosky (4) and recrystallized from 95 per cent alcohol, until free from selenious acid. The presence of selenious and selenic acids was tested by Müller's method (8), which was very satisfactory for detecting the presence of either acid in a mixture of the two.

In the following experiments, selenious acid was completely reduced to elementary selenium by adding sulfuric acid and sodium sulfite until the filtrate gave no further red precipitate; the filtrate was then tested for selenic acid.

Magnus (7) found that when elementary selenium is added to concentrated sulfuric acid in the cold, it dissolves into a greenish solution from which elementary selenium is precipitated as a red amorphous powder on dilution with water.

On the other hand, if selenium is added to hot concentrated sulfuric acid, it is oxidized to selenious acid:



With a view to ascertaining the nature of the products formed when selenium is used under the conditions which obtain in the Kjeldahl method, 0.05 gram of selenium was heated in a Kjeldahl flask over a Bunsen burner with 0.2 gram of copper sulfate-potassium sulfate mixture and 20 cc. of concentrated sulfuric acid. At the end of 15 minutes, the reaction mixture was cooled and tested for selenium and selenious and selenic acids. Positive results were obtained for only selenious acid, while both selenium and selenic acid were absent. Similar results were obtained when the copper salt (0.08 gram) of selenious acid was used instead of elementary selenium. When, however, copper selenate (0.09 gram) was used in amount equivalent to the selenium used in the authors' experiments, the reaction mixture contained both selenic and selenious acids at the end of 15 minutes' heating. Obviously the selenious acid was formed from the decomposition of selenic acid. Thus, under the above conditions, selenious acid is more stable than either selenium or selenic acid.

When the foregoing experiments were repeated with about 0.5 gram of mercuric oxide, a remarkable change was observed. Thus, in all three experiments, tests for selenium and selenious acid were negative and only selenic acid was found to be present, whatever form of selenium was added. These observations show clearly that in the absence of reducing agents, but in the presence of mercuric oxide, hot concentrated sulfuric acid converts selenium into the highest oxide while without mercuric oxide selenium added in any form is converted into selenious acid.

ORGANIC MATTER. The experiments were repeated with organic matter. In a typical instance, rice flour was employed after it had been partially digested with concentrated sulfuric acid till frothing just ceased. At this stage, portions of the digest were treated with (a) selenium, (b) copper selenite, and (c) copper selenate, respectively, in quantities equivalent to 0.05 gram of selenium, and in each case the digestion was continued for a further period of 10 to 15 minutes. In all the experiments the red amorphous form of selenium was deposited on the cooler sides of the flask, evidently through the reduction of selenious and selenic acids by the organic matter.



The digestion was stopped at this stage and cooled, after which water was added to the flasks. In (a) elementary selenium was precipitated and selenic and selenious acids were absent from the filtrate. In (b) both selenium and selenious acids were present but no selenic acid; while in (c) only selenious acid and traces of selenium were present. No selenic acid could be detected in this case.

Tests carried out on the digests obtained with the different forms of selenium and after completion of oxidation indicated in every case presence of selenious acid only. Where copper selenate was used, there were small traces of selenic acid as well.

When the experiments using partially digested organic matter were repeated with 0.5 gram of mercuric oxide, the results were remarkably different, for attempts to detect the presence of either selenium or selenious acid were unsuccessful in every case. Selenic acid was the only form in which selenium was present.

The above observations would suggest that the reaction

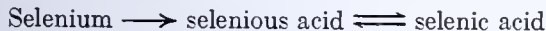


is involved and that the addition of mercuric oxide carries the reaction forward even in the presence of reducing organic matter, resulting in the formation of selenic acid, while in the absence of mercuric oxide the reaction generally proceeds in the reverse direction:

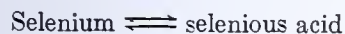


showing that under such conditions selenious acid is the most stable product.

It is therefore clear that in the oxidation of organic matter, the catalytic action of selenium in the presence of mercuric oxide is due to the reaction



The velocity of the forward reaction is so great that at no time could selenious acid be successfully detected in the reaction mixture. In the absence of mercuric oxide, another reversible reaction of the type



is brought about, enabling selenium to act as a carrier of oxygen to the reducing organic matter. But, since both selenium and selenious acid could often be detected in the mixture, this would imply that there is no pronounced difference between the velocities of the forward and reverse reactions; hence the efficiency of oxidation is much less here than when mercuric oxide is also present.

Thus it would appear that selenium acts as a catalyst in the oxidation of organic matter by virtue of setting up a rapid and reversible reaction system in the absence of mercuric oxide of the type  $\text{Se} \rightleftharpoons \text{SeO}_2$  and another of the type  $\text{SeO}_2 \rightleftharpoons \text{SeO}_3$  when mercuric oxide is present, so that oxygen is rendered active for rapid oxidation of the organic matter.

### Summary

The reactions between hot concentrated sulfuric acid and different forms of selenium, both with and without reducing organic matter, have been studied as well as the nature of the changes taking place when mercuric oxide is added.

When selenium or selenious acid reacts with hot concentrated sulfuric acid, only selenious acid is present in a stable condition. Selenic acid is slowly decomposed into selenious acid.

When the above reactions are carried out in the presence of mercuric oxide, selenium in any form is converted into selenic acid, and continues to be present as such.

In presence of reducing organic matter, and in the absence of mercuric oxide, addition of selenium to hot concentrated sulfuric acid results in the formation of small quantities of selenious acid. Selenious acid under such conditions is partially reduced to elementary selenium, while selenic acid is completely reduced to selenious acid and, to a small extent, to elementary selenium.

With the addition of mercuric oxide, however, all forms of selenium tend to exist only as selenic acid even in the presence of reducing organic matter.

When the oxidation of organic matter is complete, added selenium is present solely as selenious acid in the absence of mercuric oxide, but as selenic acid in its presence.

It is concluded that the catalytic action of selenium in the presence of mercuric oxide is due to a reversible reaction:



whereby the selenious acid acts as an efficient carrier of oxygen to the reducing organic matter. As long as there is unoxidized organic matter, the forward reaction is more rapid than the reverse reaction. When oxidation is complete, the reaction proceeds to completion in the forward direction. In the absence of mercuric oxide, another oxidation-reduction process



enables the oxidation of organic matter. There would appear to be no pronounced difference between the velocities of the two reverse reactions; hence the efficiency of oxidation is much less here than with mercuric oxide.

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# Antimony Electrode for Industrial Hydrogen-Ion Measurements

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THE continuous determination of the pH of industrial solutions over a limited range has been possible for some time, but no single electrode system has been available over the entire range for all types of solutions. When an automatic record is desired, an electrometric method offers certain advantages. A quinhydrone electrode has been described by Coons (5) for use with continuous recording potentiometers; however, this electrode is not applicable to solutions more alkaline than 9 pH. The work in the author's laboratory indicates that the glass electrode can be used to advantage in certain fields of continuous pH measurements, although it has limitations particularly in the presence of sodium, lithium, and potassium salts in the alkaline range and at temperatures in excess of 35° C., and a more reliable electrode is desirable in the alkaline range.

The use of metal-metal oxide electrode systems has appeared inviting to many investigators and many successful applications of this type of electrode are now found in the industries. The work reported in this paper was started over nine years ago.

## Requirements of an Industrial pH Electrode

It is desirable to differentiate between the nature of a high-precision pH measurement where a limit of error of  $\pm 0.01$  pH is desired and the requirements for the average industrial pH control where a limit of error of between 0.1 and 0.2 pH is probably adequate.

The more essential requirements of a desirable pH electrode for continuous industrial measurements are:

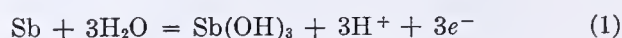
1. The electrode system should preferably be applicable over the entire range from 0 to 14 pH, yet a limited range is adequate in the majority of the applications.
2. The potential of the electrode should rapidly attain a reproducible e. m. f. value for a given pH of the solution at the electrode interface.
3. The potential of the electrode should, at the best, be only slightly affected by polarization, salt effects, oxidizing agents, reducing agents, dissolved gases, or movement of the solution at the electrode interface.
4. The electrode system should be of rugged construction.

The problem of measuring the pH of all kinds of industrial solutions by one type of electrode system is roughly analogous to the measurement of a wide variety of temperatures with one form of thermometer. It is expecting a great deal from one electrode system. There are a great many factors entering a true pH measurement, but the industrial control is generally more dependent on a reproducible record of pH than on academic correctness.

## Variable Factors of a Metal-Metal Oxide Electrode

The theory of metal-metal oxide electrodes has been briefly discussed by Clark (4), Britton (2), Getman and Daniels (6), and Kolthoff and Furman (7).

No extensive theoretical discussion seems necessary; however, the e. m. f.-pH relationships for metal-metal oxide systems have been expressed by Roberts and Fenwick (9) as follows:



for which the e. m. f. expression will be

$$E = E_0 - \frac{RT}{3F} \ln \frac{(\text{Sb}(\text{OH})_3)(\text{H}^+)^3}{(\text{H}_2\text{O})^3} \quad (2)$$

Britton's (2, p. 80) viewpoint seems to lead to a better understanding:

$$E = E_0 - \frac{RT}{F} \log K_w + \frac{RT}{nF} \log K_s + \frac{RT}{F} \log (\text{H}^+) \quad (3)$$

where  $K_s$  refers to the solubility product of the sparingly soluble metal compound. Hence, the activity of the water must remain constant and the solution must remain saturated with oxide if the following holds true:

$$E = \text{constant} + \frac{RT}{F} \log (\text{H}^+) \quad (4)$$

It is well recognized that the use of a metal-metal oxide electrode depends upon the presence of metal ions in solution from some well-defined source other than the metal itself. A desirable source is a sparingly soluble hydroxide.

The significance of the factors affecting the potential of a metal-metal oxide electrode has not always been fully appreciated. Equation 3 indicates that the potential of a metal-metal oxide electrode is a function of the temperature, the hydrogen-ion concentration, the solubility product of the sparingly soluble hydroxide, the activity of the water, and the electromotive activity of the metal. Some of these factors are influenced by gas and ion adsorption, the type of oxide, foreign oxidation or reduction systems, and the nature or concentration of the salts in solution. Therefore, a considerable number of variables must be carefully controlled before reproducible results can be expected with a metal-metal oxide electrode. The choice of a fundamentally sound metal-metal oxide system does much in the control of these factors.

## Choice of the Metal-Metal Oxide

Because of certain conflicting statements in the literature it seems desirable to review some of the important aspects of this problem. A readily oxidized metal is desired. If the metal is attacked by acid or alkali with the subsequent formation of hydrogen, a combination of a gas electrode and the metal-metal oxide electrode is the resultant. Hence those metals less electronegative than hydrogen are the most applicable for wide-range operation. However, not all of the metals less electronegative than hydrogen are inviting; it is not the metal which is the fundamental factor, but rather the oxide or a proper sparingly soluble compound of the metal.

If the oxide is to be the source of the metal ion, the fundamental equation assumes that the solubility of the oxide is so small that it does not affect the hydrogen-ion concentrations over the working range of e. m. f. measurements. In other words, the metal oxide must be very sparingly soluble in both acids and alkalies.

The following oxides are those worthy of preliminary consideration: antimony, trioxide, arsenic trioxide, bismuth trioxide, columbium pentoxide, tantalum pentoxide, tungsten trioxide, chromium trioxide, molybdenum trioxide, and tellurium trioxide. Unfortunately, few exact solubility figures for these oxides are available, but by a study of other factors the metal-metal oxide systems may be narrowed to a consideration of a very small number of elements.



Many metals which have been used for electrode measurements tend to form a surface coating and the nature of many of these coatings has been uncertain. This fact has been ignored in many published accounts. This type of reaction has been erroneously attributed to gas-metal potentials by some investigators. If the action of water upon the oxide produces a hydroxide which is appreciably soluble, the resultant potential at the metal interface will be influenced by the hydroxide.

In order to obtain a qualitative idea of the influence of dissolved oxides upon metal-metal oxide potential measurements, purified oxides were shaken several times with distilled water. The first three lots of water were decanted and the measurements were made upon the fourth extraction. The glass-saturated-calomel electrode system was used to determine the pH of the original water and of the oxide suspensions. The final measurements were made while the oxide was held in suspension by rapid stirring. Table I gives the results of the tests for 0.1 gram of the oxide suspended in 100 ml. of water and in contact with air.

The data of Table I indicate that the use of many oxides as a source of hydroxide in metal-metal-ion electrode measurements will involve serious errors, particularly in unbuffered solutions. This is a limitation to be considered in the use of the metal-metal oxide type of electrode.

TABLE I. CHANGE IN pH OF DISTILLED WATER BY ADDITION OF OXIDES

(Glass-saturated-calomel electrode measurements. Solution in contact with air and stirred. Temperature 23° to 25° C.)		
Oxide Added	pH Change	Direction of Change
Sb <sub>2</sub> O <sub>3</sub>	0.00	Neutral
Sb <sub>2</sub> O <sub>5</sub>	0.47	Acidic
Bi <sub>2</sub> O <sub>3</sub>	0.10	Basic
CuO	0.69	Basic
Ag <sub>2</sub> O	3.40	Basic
HgO	0.35	Basic
WO <sub>3</sub>	1.14	Acidic
Cr <sub>2</sub> O <sub>3</sub>	0.10	Acidic
Cb <sub>2</sub> O <sub>5</sub>	0.00	Neutral
Ta <sub>2</sub> O <sub>5</sub>	0.00	Neutral
TeO <sub>3</sub>	1.08	Acidic

Apparently the number of metals and metal hydroxides which are available for the construction of a stable metal-metal oxide electrode adaptable to the range of 0 to 14 pH is limited. Mercury, columbium, and chromium may offer possibilities, if the metal surface can be maintained in equilibrium with the proper insoluble compound. Its moderately low melting point, amphoteric characteristics, and ease of electrolytic purification give antimony an advantage over the other metals.

Although there may be a question as to the existence of the various antimonious acids, there is another chemical equilibrium which may occur in the solution, which results in the formation of a sparingly soluble antimony compound. We may have a reaction of the following general type:



Milbauer and Slemr (8) found that at room temperature metallic antimony was oxidized when submerged in water, but if tartrates or citrates were present the oxidation was greatly increased. Ruff and Albert (10) found that antimony was attacked by solutions of alkalis and their salts. Clark (3) showed that neutral hydrogen peroxide was without action on antimony, but in the presence of alkali an antimonate was formed.

Evidently in aqueous solutions in contact with air there may be an ample source of an insoluble antimony compound from the interaction as indicated by Equation 5. This confirms the observations of other investigators that the addition of oxide to aqueous solutions is not required for an industrial electrode of moderate accuracy.

Antimony Metal

It seems desirable to present a brief summary of the development of a practical form of antimony electrode. One important phase of this work involved the purity of the metal. The data of Table II were obtained upon electrodes cast in the form which was finally adopted.

TABLE II. EFFECT OF METAL PURITY UPON ANTIMONY ELECTRODE POTENTIAL

Make of Antimony	Impurities				Antimony-Saturated-Calomel Electrode at 25° C.	
	Fe	As	Sn	Pb	3.8 pH buffer	10.7 pH buffer
	%	%	%	%	E. m. f. (volt)	
B.	0.015	Trace	...	0.010	0.2096	0.5846
P.	0.010	0.050	0.007	...	0.2158	0.5938
L. & N. electrolytic	000	000	000	000	0.2161	0.5982

Work upon the relative merits of the castings with the B. antimony as compared to the L. & N. electrolytically prepared metal on continuous recording tests showed that in a 2.58 pH buffer, as well as in a 7 pH buffer solution, the metal with small amounts of impurities tended to be less stable in the acid range than the pure electrolytic metal. The presence of small amounts of copper in the metal causes distinct errors.

The possibility of plating antimony upon platinum or gold wires was studied at great length. Some investigators in this field considered that the method of Shukov and Awsejewitch (11) gave permanence, reproducibility, and exact linearity over the whole pH range. Their method consisted in electroplating antimony on amalgamated platinum wires from a 25 per cent antimony trichloride solution in acetone.

Anhydrous antimony trichloride was dissolved in a large number of ionizing solvents. The solvents for antimony trichloride which were studied as electrolytes for the metal deposition were water, acetonitrile, nitrobenzene, methyl alcohol, acetone, lactic acid, amyl alcohol, ethyl acetate, and furfural. The best deposits resulted from solutions in acetonitrile, but very good results were obtained in the methyl alcohol and the acetone solutions.

Antimony salts are so easily hydrolyzed in aqueous solutions that care must be exercised to prevent contamination of the deposit with basic salts. All attempts in which aqueous solutions were used to build up a heavy antimony deposit resulted in nonadherent or very black deposits of antimony.

The electrodes of antimony electroplated upon platinum checked very well among themselves, yet their potential was somewhat lower than the ordinary cast-antimony electrode. The electroplated electrode was found to hold its potential for only 5 to 8 hours in a 10.8 pH buffer which was in contact with air and which was in continuous circulation. However, owing to the solubility of the antimony, the life of such an electrode is short. A serious drift begins after about 10 hours of continuous operation when a portion of the base metal becomes exposed sufficiently to set up auxiliary reactions of the air-electrode type.

Because of the comparatively high solubility of antimony in solutions containing dissolved oxygen or air, the electroplated type of electrode is not inviting for continuous measurements, although it may be used for a limited number of indicating measurements.

It was evident that a form of electrode must be employed which had an appreciable thickness of metal to withstand the gradual solvent action caused by continued use. A supply of pure metal was also required. Accordingly, the preparation of electrolytic metal was undertaken.

Antimony trioxide which had been purified by solution in hydrochloric acid and reprecipitation with sodium carbonate was



dissolved in hydrofluoric acid. A 12 per cent solution of antimony fluoride was used. Electrolytic antimony was deposited from this solution at a platinum electrode. A platinum anode of 20-sq. cm. surface was immersed within an extraction thimble compartment containing an excess of antimony oxide. A platinum cathode of 1-sq. cm. surface was used. A current of 5 amperes produced excellent crystals of antimony which settled on the bottom of the container. This metal was washed, dried, and melted and was then ready for final casting and assembly.

### Methods of Mounting Antimony

A metal electrode involves not only a metal surface in contact with the solution, but also some means of making electrical contact between the metal surface and the potentiometer.

A great many types of electrodes were made and certain objections were found to most of these. Figure 1 shows a few of the types which were studied.

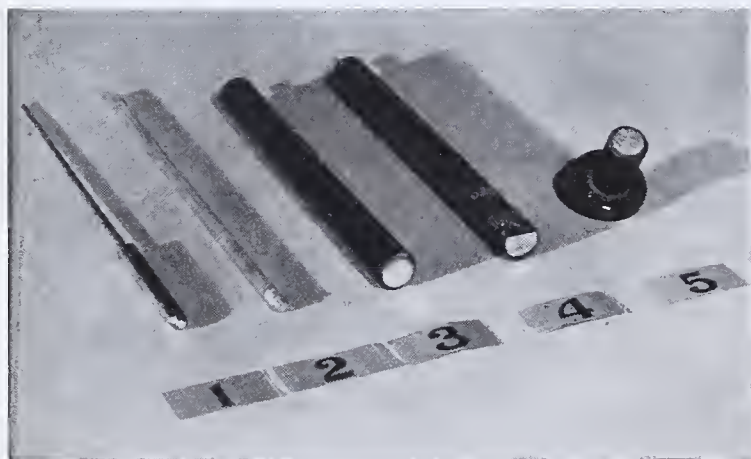


FIGURE 1. TYPES OF ANTIMONY ELECTRODES

No. 1 is a plain antimony metal stick, into which a metal connection had been threaded. This type of electrode behaved erratically on continued use, as a uniform metal surface could not be maintained. No. 2 consists of antimony fused within a glass tube. The active lower end is ground flat and polished. Connection to the external circuit is made through a layer of mercury resting on the top surface of the antimony. This electrode was found to give erroneous results on continuous operation due to occlusion of impurities at the glass-antimony metal seal. Nos. 3, 4, and 5 illustrate the general design of an electrode formed by molding rubber around an antimony casting connected to an external lead wire. The exposed bottom metal surface is ground and polished to a uniform smooth surface. No. 4 shows a section of the mounting, while No. 3 and No. 5 show types of finished commercial antimony electrodes. A rugged type of electrode has been produced.

### Basis for Choice of Electrode Form

The molded form of antimony electrode appears to be superior to other types because of three primary considerations.

1. The active electrode surface is completely immersed in the solution. This prevents secondary reactions where the metal

enters the solution, as may be the case where a plain stick of antimony is used. The author believes that continuous measurements using an unprotected stick of antimony give erroneous results.

2. The active portion of the metal surface is flat and the exposed metal surface has no rough edges or crevices, which may collect sediment from the liquid. Secondary potential effects are thereby prevented. The antimony metal is slowly etched and from time to time it is necessary to resurface the exposed metal in order to reduce absorption errors. It is essential that the wire lead and the upper portion of the metal be protected from the action of the solution.

3. An electrode assembly is obtained which can withstand rough usage in the industrial field.

Information as to the most desirable size of metal surface, the influence of annealing, and the relative effect of a polished and sandblasted surface was also obtained. The area of the exposed metal surface which is required is governed by the conductance of the solutions in which the measurements are to be made. The larger the exposed surface, the lower is the sensitivity of the galvanometer required in the potential measurement. The author adopted an exposed surface 13 mm. in diameter for average conditions. His tests on the value of annealing at 573° C. indicated that there was little advantage in this treatment for commercial electrodes.

Beilby (1) has shown that the flowed layer of a metal on a polished surface is vitreous rather than crystalline. When the solutions are in contact with air the polished antimony surface becomes etched within a short time. Hence, for continuous e. m. f. measurements there is apparently little difference between starting with a polished or rough surface, if an adequate time is provided for the surface equilibrium and oxide formation to be established. However, the scratched sections of an antimony surface are the first to be etched and the deep crevices may hold sparingly soluble salts and introduce false potentials. Accordingly, it is wise to utilize an initially polished surface and thereby provide an even crystal etching. The polished surface must be etched by solution immersion, preferably in a 7 to 9 pH buffer for an hour or two prior to use.

Over five hundred different industrial recording pH installations now utilize the molded antimony electrode.

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# Characteristics of the Antimony Electrode

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A STUDY of the methods of making a desirable form of industrial antimony electrode has been presented in the previous paper (1). The work discussed in the present paper was carried out with a molded hard-rubber flat-surface type of antimony electrode, using a saturated-calomel reference electrode in all the tests.

## Essential Factors

The e. m. f.-pH relationships of the antimony electrode are influenced by several factors, a knowledge of which makes it possible to employ this electrode to distinct advantage in the continuous recording of the pH of industrial solutions. The stability and the limit of error of the e. m. f. measurement depend upon (1) the nature of the electrode surface, (2) the concentration of dissolved air or oxygen, (3) the agitation prevailing at the electrode surface, (4) the nature and concentration of the dissolved salts, and (5) the temperature of the system.

By proper standardization of these variables, it is possible to obtain continuous pH measurements well within the limit of error demanded by the average industrial application. With proper maintenance a reproducibility of  $\pm 0.15$  pH may be obtained.

## Nature of Electrode Surface

Whenever an antimony electrode is immersed in an aqueous solution that is saturated with air at approximately 25° C., a slow etching action occurs whereby the crystalline nature of the antimony becomes clearly evident after approximately 24 hours of immersion. The e. m. f. of the electrode system gradually drifts until the electrode surface has become thoroughly etched. At least sufficient amounts of a reproducible and sparingly soluble antimony compound must be formed to set up an equilibrium involving the antimony ion. When an electrode with a polished antimony surface is immersed in an aqueous solution free from dissolved oxygen or air, there is very little change in the nature of the surface. This is in great contrast to the case where dissolved oxygen or air is present. The higher the dissolved oxygen content the more rapid is the etching reaction.

Long-continued use of an antimony electrode in aqueous solutions that are in contact with air results in a surface that is deeply etched. The etching becomes deepest at points of abrasion. Initially smooth surfaces are desirable. A too deeply etched antimony surface tends to occlude impurities and it is then necessary to repolish.

In order to avoid uneven corrosion or excessive secondary reactions, it is desirable to wipe off the antimony electrode surface after 24 hours of continuous service. It is essential to pretreat the polished antimony surface prior to use, in order to secure the proper type of sparingly soluble antimony compound.

An extensive series of automatically cleaned electrode tests has been carried out in order to establish the influence of maintaining a surface which was always free from secondary reaction products. An automatically operated surface cleaner is helpful in certain cases where crystalline salts tend to separate out of the solution or where secondary reactions occur, but is not essential for many commercial applications.

## Concentration of Dissolved Air or Oxygen

The e. m. f.-pH relationship of the antimony-saturated-calomel electrode system depends upon the oxygen concen-

tration in the solution. The potential of the pretreated system when buffers were saturated at 25° C. with various gases, and when the solution was constantly stirred, was found to be as follows:

Saturating Gas	3.95 pH Volt	6.91 pH Volt	11.04 pH Volt
Nitrogen	0.261	0.416	0.655
Air	0.224	0.398	0.622
Oxygen	0.201	0.375	0.594

The stability of the electrode in 3.95 pH buffer in the presence of nitrogen gas is not good. There is always a tendency to drift to lower voltage values on continued operation.

The author's studies indicate the following millivolt change per pH change at 25° C. for the antimony-saturated-calomel electrode system:

Saturating Gas	4.0 to 7.0 pH Volt	7.0 to 11.0 pH Volt
Nitrogen	0.052	0.058
Air	0.059	0.051
Oxygen	0.059	0.050

The Nernst equation at 25° C. indicates that there should be a change of 0.0591 volt per pH change.

The tendency towards instability in the acid range when the dissolved oxygen concentration is low and the failure of the electrode to follow the Nernst equation in the alkaline range when dissolved oxygen is present are characteristics of the antimony electrode. The relative ease of oxidation of the antimony in the alkaline range produces secondary products at the metal interface with the result that the equilibrium conditions are disturbed. In the acid range, in the absence of any dissolved oxygen, the amount of antimony oxide maintained at the metal interface is inadequate to establish equilibrium conditions.

## Agitation at Electrode Surface

The e. m. f.-pH relationships of the antimony-saturated-calomel electrode system depend upon the condition of the solution at the metal-solution interface. When the solution is agitated, the e. m. f. of the air-saturated system is different from that when there is no motion at the electrode interface. However, a small agitation at the electrode surface has nearly the same disturbing influence as a vigorous agitation.

The extent of the influence of agitation depends upon the pH, the temperature, and the nature of the solution, and the concentration of dissolved oxygen.

When a buffered solution is saturated with air at temperatures below 15° C., there are only small differences between the readings in agitated and nonagitated solutions over the range of 4 to 11 pH. The influence of agitation is more critical in the case of a solution with a very low salt content. Certain salts, such as citrates or tartrates, favor a greatly increased solubility of antimony metal by oxygen, as well as an increased solubility of the oxide, and these present exceptions to the general case. As the temperature is raised above 15° C., the higher the temperature the greater is the difference between the agitated and nonagitated readings, but with moderately well-buffered solutions below 9.0 pH the error is less than 0.1 pH even at 45° C. In any instance, the non-agitated solution approaches the true equilibrium potential in accordance with the Nernst equation for the particular pH and temperature condition.



Stable e. m. f. readings for the antimony-saturated-calomel electrode system were obtained while the buffer solution was agitated in contact with air with a mechanical stirrer. The stirring was stopped and after 5 minutes another set of readings was taken. The following gives a qualitative idea of the differences noted:

	3.95 pH	6.91 pH	11.04 pH
35° C.	5-mv. rise	5-mv. rise	15-mv. rise
25° C.	2-mv. drop	No change	12-mv. rise
10° C.	3-mv. drop	2-mv. drop	2-mv. drop

However, when buffer solutions are saturated with pure oxygen rather than air, very stable readings are obtained over the temperature ranges of 10° to 35° C. and for ranges of 4 to 11 pH. When using oxygen, the difference between agitated and nonagitated readings is not greater than 0.1 pH over the whole range. This fact is particularly interesting since the slope of the e. m. f.-pH curve with alkaline solutions saturated with oxygen does not follow the Nernst equation. The author's data show that a very reproducible pH electrode results when using a properly designed antimony electrode in solutions saturated with oxygen. This system may be applied to a wide range of pH and the results are not greatly affected by the agitation of the solution, at least over the temperature range of 10° to 40° C.

Considerable differences were noted between the readings for agitated and nonagitated buffer solutions which were saturated with nitrogen in the range of 3 to 7 pH. The differences were smaller in the 7 to 11 pH range. Acid solutions with a deficiency of dissolved oxygen cause an unfavorable operation of an antimony electrode after a few hours of immersion.

The author feels that any condition favoring the reduction of dissolved oxygen in acid solutions, such as temperatures above 40° C., saturation with nitrogen, or the presence of certain salts, tends to give the most pronounced differences between the e. m. f. measurements of the antimony-saturated-calomel electrode system in agitated and nonagitated solutions. Since antimony metal is soluble in aqueous solutions in the presence of dissolved oxygen, there is a tendency to reduce the oxygen concentration of the solution close to the antimony surface. The oxygen depletion is less in acid solutions than in alkaline solutions. Secondary reactions in the alkaline range involving antimonates will change the normal equilibrium conditions. The use of a nitrogen atmosphere in the alkaline range limits this oxidation. When using a nitrogen atmosphere, it is necessary to employ an electrode surface which has been etched by the interaction of dissolved oxygen and thereby has an excess of sparingly soluble antimony compound at the metal-solution interface. An excess of antimony trioxide is desirable in alkaline solutions which are saturated with nitrogen. A continuous movement of solutions past the metal surface produces an unsaturated surface condition unless more oxygen is available to oxidize more of the antimony metal.

When a high concentration of oxygen is available, as at low solution temperatures or in the presence of an oxygen atmosphere, there is sufficient oxidation at the metal surface to ensure saturation, and sufficient excess of dissolved oxygen present at all times to continue the equilibrium conditions even for rapid flows of fresh solution past the electrode surface, as is the case when the solution is agitated. Equilibrium conditions are not obtained when dealing with alkaline solutions saturated with air, since the partial pressure of oxygen is too low to supply all the oxygen required for the various reactions which occur with a continuously changing solution at the metal surface. However, this results only in a change in slope of the e. m. f.-pH curve. This also indicates why those solutions which are saturated with oxygen gas show small differences between the agitated and nonagitated condi-

tions, while the alkaline solutions saturated with air are responsive to agitation.

### Nature and Concentration of Dissolved Salts

The basic equation for a metal-metal ion electrode involves a consideration of the activity of the water and the solubility of the oxide. As expected, the antimony electrode exhibits definite salt effects.

An e. m. f.-pH relationship may be obtained by the use of certain well-known buffer solutions which will apply to a large number of industrial solutions. Such buffers as potassium hydrogen phthalate, mixtures of this with hydrochloric acid or sodium hydroxide (Clark and Lubs), sodium acetate and hydrochloric acid mixtures (Walpole), primary potassium phosphate and sodium hydroxide mixtures, disodium phosphate and primary potassium phosphate mixtures (Sørensen), boric acid and sodium hydroxide mixtures (Clark and Lubs), and disodium phosphate and sodium hydroxide mixtures (Ringer) have been used to obtain an e. m. f.-pH relationship over the range of 3 to 12 pH and for temperatures from 10° to 70° C., and consistent results have been obtained over the above pH range. These solutions have a specific resistance at 25° C. varying from 100 to 300 ohms. This feature will be discussed in connection with temperature coefficients.

When the calibration curve obtained with the above solutions is used with buffer solutions containing tartrates, citrates, oxalates, or phenyl acetic acid (the Prideaux and Ward buffer), there may be a wide divergence over the 3 to 12 pH range at 25° C. Since this error does not involve the  $RT/F$  pH term, or slope portion of the fundamental equation, it is possible to make a constant correction. The influence of temperature upon these solutions is markedly different from that on the previously mentioned buffer solutions. Reproducible results are obtained in solutions containing these disturbing salts, yet a special calibration curve must be used. The use of many so-called universal buffers involves the above error.

When dealing with water solutions in which the salt concentration is low, such as the average city water in the eastern United States, the calibration curve obtained by the first mentioned group of buffers has been found to give erroneous results. It is necessary to use a different type of e. m. f.-pH relationship for solutions of low salt content, yet for these specific conditions reproducible results may be obtained. The specific resistance of this type of solution varies from 3000 to 20,000 ohms at 25° C.

An e. m. f.-pH curve based upon buffers free from citrates, tartrates, etc., has been used in many industrial types of recording pH installations since 1932. As the constituents of a given type of application remain fairly constant, it is possible to make an initial correction for any specific application, by making a supplementary indicating pH measurement with a hydrogen gas electrode or its equivalent. The deviation is thus originally obtained and the recording equipment may be set to correct for the specific salt effect. Reproducible results within  $\pm 0.1$  pH over the whole pH range will result just as long as the general nature of the solution does not change.

We should not expect that the antimony electrode would respond only to pH changes in the presence of oxidation-reduction potentials and such is the case. However, fairly reproducible results have been obtained in the presence of mild oxidizing agents as well as mild reducing agents. Dilute solutions of hydrogen peroxide, potassium permanganate, and sodium chromate cause disturbing secondary reactions. In these cases, a low pH value results when using an antimony electrode. However, the electrode behaves in a normal



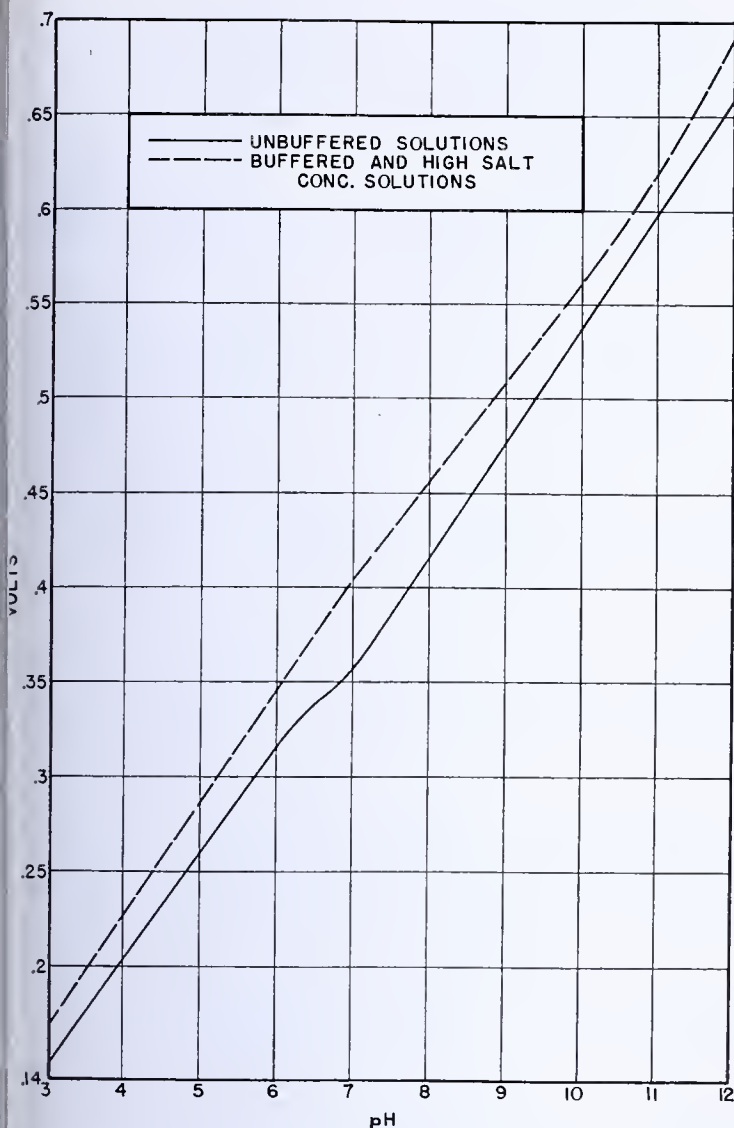


FIGURE 1. E. M. F.-pH FOR ANTIMONY-SATURATED-CALOMEL ELECTRODE SYSTEM  
Solutions saturated with air at 25° C. and in motion

manner in solutions with a residual chlorine content of as much as 0.5 part per million. It was found that the antimony electrode recovered from the abnormal effects of oxidizing agents after these had been removed. Good results have been obtained in dilute solutions of sodium sulfite and sodium sulfide.

The continuous use of the antimony electrode in solutions more alkaline than 10 pH with a sodium content in excess of 0.1 molar results in a slow but gradual deposition of white crystals (probably sparingly soluble sodium antimonates) on the antimony surface. The error is not great, but unless these crystals are occasionally removed, an abnormally high pH reading will result.

Even traces of copper in solution involve a limitation of the antimony electrode. The presence of copper in solutions coming in contact with an antimony electrode establishes secondary reactions which result in abnormal potentials, which would be interpreted as low pH values for a given solution. The presence of 0.5 part of copper per million in a 0.92 pH buffer causes an immediate error of 0.2 pH. When one part of copper per million is present, the coating of copper on the antimony surface may be clearly seen within a half hour after immersion. Apparently there are two types of error: an oxidation-reduction error which occurs immediately, and a secondary copper-copper-ion potential which increases with increased immersion of the electrode. A given concentration of copper produces a greater error the more acid

the solution. Accurate results can be obtained on continuous recording installations only when the copper content of the solution is below 0.1 part per million. Fortunately, the solubility of copper in solutions more alkaline than 7 pH is so low that we encounter little trouble in this range of application; however, in the acid range the presence of mere traces of copper may be serious.

Solutions of metals less electropositive than antimony will behave like copper solutions. In other words, when we get immersion deposition of some other metal on the antimony surface, we are no longer involved with an antimony electrode.

A systematic study of the many possible salt errors of the antimony electrode has been undertaken, but this forms material for a separate paper.

### Influence of Temperature

The temperature coefficient of the antimony electrode has been determined when the electrode is used in the series of air-saturated buffers mentioned in the preceding section. The coefficient of the antimony-saturated-calomel electrode system varies with the pH value of the buffer and is of the order of 0.00115 volt per 1° C. at 3 pH, 0.00210 volt per 1° C. at 7 pH, and 0.00344 volt per 1° C. at 12 pH. The temperature coefficient for unbuffered solutions is different from that of buffered solutions.

As the problem of temperature coefficients is somewhat involved, yet of great importance to the interpretation of the e. m. f. values of the antimony electrode, this subject will be presented in a separate paper.

### Industrial Applications

The use of air-saturated solutions for the continuous recording of pH is more practical than the use of oxygen-saturated solutions. The author's early results indicated that it was possible to diagnose the average industrial conditions and to apply the proper calibration curve.

When dealing with an industrial solution, a calibration curve may be based upon that obtained with the buffers mentioned in the section on the nature and concentration of dissolved salts. For the antimony-saturated-calomel electrode system, used in agitated buffer solutions saturated with air at 25° C., this follows the general relationship:

$$\begin{array}{ll} \text{From 3 to 7 pH} & E = -0.008 + 0.059 \text{ pH} \\ \text{From 7 to 11 pH} & E = +0.050 + 0.051 \text{ pH} \end{array}$$

When involved with low salt concentrations as in many water-treatment applications at 25° C., a different relationship results:

$$\begin{array}{ll} \text{From 3 to 6 pH} & E = -0.024 + 0.056 \text{ pH} \\ \text{From 6 to 8 pH} & \text{A nonlinear relationship} \\ \text{From 8 to 11 pH} & E = -0.071 + 0.060 \text{ pH} \end{array}$$

Figure 1 shows the e. m. f.-pH relationships at 25° C. for air-saturated solutions.

Most industrial solutions are in contact with air, and generally information is available as to their nature and salt content; hence, it is relatively easy to apply the correct scale law for any given application. It is possible to supply a recording potentiometer with a manually adjustable rheostat in order to fix the scale to an exact value at the most important point on the pH range. In the absence of the chief disturbing features, such as oxidation-reduction potentials or copper, a pH measurement reproducible to  $\pm 0.15$  pH may be obtained, provided reasonable consideration is exercised in the choice, installation, and care of the electrode system. Oxidation-reduction potentials or copper poisoning are present in a distinct minority of industrial applications.



The antimony electrode has given satisfactory industrial performance in widely different types of commercial applications, such as in sugar-mill liquors, paper-mill solutions, water-treatment systems, aqueous starch suspensions, various silicate solutions, clay suspensions, sulfite solutions, phosphate solutions, ammonium hydroxide solutions, lime treatment, soda ash neutralization, alum solutions, beer, etc.

The antimony electrode is rugged. Since the antimony-saturated-calomel electrode system represents a relatively low electrical resistance type of pH measuring equipment, the problems of electrical pickup and leakage are practically absent. An antimony electrode with a properly prepared sur-

face responds immediately to any changing pH condition of a solution. Particularly in applications where there is high humidity, high temperature, or high alkalinity, the antimony electrode seems to have advantages for continuous recording pH measurements.

Best results with the antimony electrode require a good understanding of the fundamentals and specific characteristics of this electrode system, which is believed to have a definite place in the industrial field.

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# Determination of Ascorbic Acid

## Electrometric Titration Method

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UNTIL recently no chemical method for the determination of vitamin C has proved adequate in the presence of colored pigments. A new method using 2,6-dichlorophenol-indophenol in electrometric titrations is presented herewith.

In making vitamin C determinations on fruits and vegetables the titration method of Tillmans (10), as modified by Bessey and King (2) and Mack and Tressler (7), has been used extensively. These authors titrate the ascorbic acid with 2,6-dichlorophenolindophenol. The complete oxidation of the ascorbic acid is indicated by a change in the color of the solution titrated from colorless to a faint pink in the acid solution. This color change is obscured in juices with a natural red or pink pigment. The animal assay method can be employed in such cases, but it is expensive, must be continued through a long time interval, is not sensitive to small differences in concentration, and is not applicable to many problems where titration methods can be used satisfactorily.

Since the present investigation was completed, two publications (1, 4) have appeared describing the use of the photo-electric colorimeter which also can be used in determinations on colored extracts. The chief difficulty in most of the methods of determination lies in the fact that the oxidizing agents are nonselective and will oxidize compounds other than ascorbic acid. The 2,6-dichlorophenolindophenol dye seems to have a high specificity for reduction by vitamin C. Very few other compounds react rapidly with the dye in acid solution. Since this dye is considered a satisfactory indicator for the estimation of vitamin C in colorless extracts, a method employing it in pigmented solutions where the end point is masked was considered advantageous. The color change at the end point in the titration with the dye is accompanied by a decrease in oxidation-reduction potential; hence a variation in e. m. f. should be easily measured by means of suitable equipment. This is possible with an electrometric titrimeter such as the one used in the present investigation (5).

### Methods Used

The electrometric titrimeter can be used in two ways. If the qualitative unit is used alone, the end point of the reaction is indicated by a distinct blink of the electric eye. A titration curve can be plotted using the quantitative unit.

Both methods were employed in the titrations with 2,6-dichlorophenolindophenol and with iodine.

When the indophenol dye was used to oxidize the ascorbic acid, no definite blink of the electric eye of the titrimeter was noticed; the change in the oxidation-reduction potential during the reaction was so slow that it caused no pronounced movement of the eye with either the platinum-platinum electrode or the platinum-tungsten electrode.

Titrations were repeated using the quantitative unit. Readings were taken at regular intervals during the process of oxidation of the ascorbic acid in the dye titration, and the curve was plotted. The addition of dye causing the first large change of potential was taken as the end point of the reaction. This point was easily found by plotting the difference between consecutive readings.

The Stevens iodine method (9) was also tried on the titrimeter. The visual color change coincided exactly with distinct closure of the eye, giving a definite end point. No titration curve could be obtained, since a back-titration was used. However, the curve was unnecessary, since a distinct end point could be found more quickly with the blink of the eye using only the qualitative unit. Frequent standardization of the iodine and thiosulfate was unnecessary, but the dye

TABLE I. ASCORBIC ACID CONTENT OF VEGETABLES

Vegetable	Visual Titration Mg./g.	Electrometric Titration		Iodine Titration	
		Mg./g.	Difference from visual titration	Mg./g.	Difference from visual titration
			%		%
Yellow Tomato		0.245	+7.0	0.288	+25.8
Yellow Plum	0.229	0.269	-1.8	0.320	+16.8
Golden Queen	0.274	0.185	+2.2	0.263	+45.3
Ripley	0.181	0.285	-0.7	0.353	+23.0
Yellow Marigold	0.287	0.213	0.0	0.203	-4.7
Golden Ball	0.213				
Golden Dwarf					
Champion	0.206	0.194	-5.8	0.253	+22.8
Peas (frozen)	0.130	0.130	0.0	...	...
Kale, German Dwarf					
(leaf)	1.170	1.160	-0.9	...	...
Spinach, New Zealand	0.192	0.199	+3.6	...	...
Lettuce					
Iceberg	0.102	0.096	-5.9	...	...
Mignonette	0.109	0.105	-3.7	...	...
Lemon juice	0.352	0.349	-0.9	...	...
Orange juice	0.348	0.365	+4.9	...	...



used was standardized daily by the thiosulfate method as described by Buck and Ritchie (3).

As seen in Table I, the iodine method gave higher results for the vegetables tested than did the visual dye titration. This was in agreement with the results obtained by Stevens, but the method could be used for following the relative retention of vitamin C in different methods of processing any given fruit.

### Recommended Method

From this study, the method found most satisfactory for the determination of ascorbic acid in deeply pigmented extracts was the use of the electrometric titrimeter with 2,6-

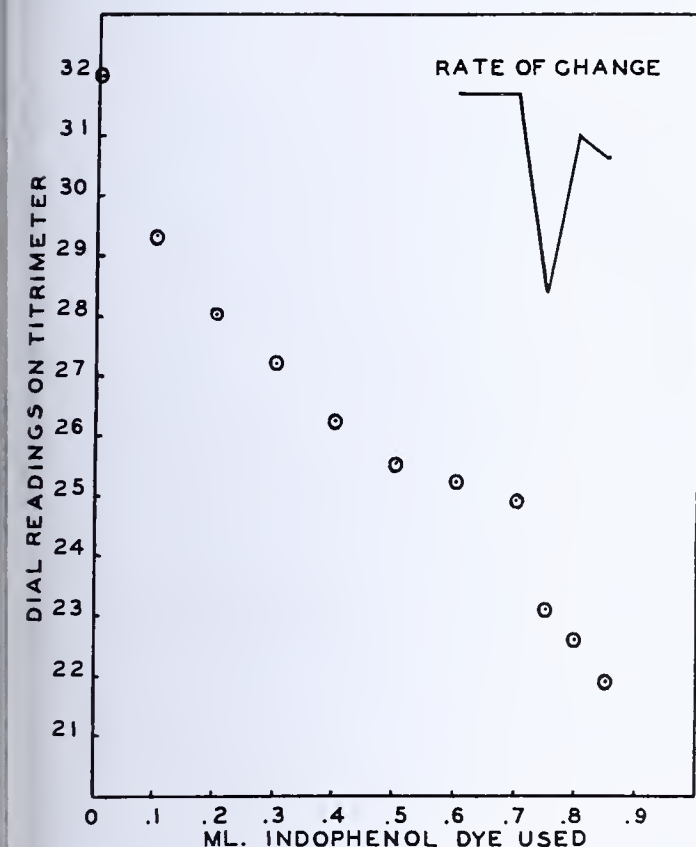


FIGURE 1. DETERMINATION OF ASCORBIC ACID

chlorophenolindophenol to determine points on a titration curve. A platinum-tungsten electrode stirrer was found to be more sensitive than a platinum-platinum electrode in the determination of the potential.

Extracts were made of peas, kale, lettuce, and spinach by placing weighed samples in mortars containing 30 cc. of the extracting solutions, and grinding with acid-washed sand. They were centrifuged for at least 5 minutes and the supernatant liquid was poured off into 100-cc. volumetric flasks. Washing of the material was repeated with 30-, 20-, and 20-cc. portions of the fresh extracting solution. The extract was made up to volume with distilled water. Tomatoes were run through a Sep-ro-siv equipped with a 20-mesh screen instead of grinding with sand. This removed skin and seeds. Although only 75 cc. of the extractant were used with 25 cc. of the pulpy tomato juice, four extractions were made. Sulfuric acid (N, 5 per cent) was used in the case of tomatoes, lettuce, and spinach, while 8 per cent dichloroacetic acid was used for peas and kale. As suggested by several workers (6, 7, 8), 2 per cent metaphosphoric acid was used in all acid extractants to prevent catalytic oxidation of ascorbic acid. Varying concentrations of ascorbic acid dissolved in 1 per cent acetic acid were tested as checks, using both the usual titration and electrometric titration methods.

For titration with the titrimeter, a 10- or 20-cc. aliquot of the extract was transferred into a 50-cc. beaker and about 25 cc. of 1 per cent acetic acid were added to increase the volume. Dye was added in 0.1-cc. aliquots until the end point was approached, after which 0.05-cc. portions were added. Readings were taken

TABLE II. DETERMINATION OF PURE ASCORBIC ACID

Visual titration, mg./100 cc.	1.54	2.38	3.14	4.19
Electrometric titration, mg./100 cc.	1.57	2.52	3.32	4.29
Difference, %	+1.95	+5.88	+2.55	+2.39

on the titrimeter about 15 seconds after each addition; if taken immediately or much after 15 seconds, reliable results were not obtained. The titration curve was plotted and the first large change of potential found. Figure 1 is a typical curve. The rate of change of readings on the titrimeter dial appears at the top of the graph. The results of the visual dye titration and electrometric titration methods agree to within experimental error for both vegetables (Table I) and pure ascorbic acid (Table II). Dilution of the dye results in more accurate determinations.

Since the method was proposed for colored extracts, some work was also carried out with strawberry juice. The color made visual titration difficult, but results obtained with very dilute solutions agreed with titrimeter results. The titrimeter gave 0.489 mg. of ascorbic acid per cc. of juice, while visual titration gave 0.495 mg. of ascorbic acid per cc.

In order to test the specificity of the titrimeter method for vitamin C, some of the strawberry juice was filtered through Norite. This oxidized the ascorbic acid to dehydroascorbic acid which does not reduce the dye. Known quantities of ascorbic acid were added to 10 cc. of this oxidized juice plus 10 cc. of 10 per cent metaphosphoric acid. Titration showed that the presence of oxidizing or reducing agents found in the juice did not interfere with the end points. Results are given in Table III.

TABLE III. DETERMINATION OF ASCORBIC ACID ADDED TO OXIDIZED STRAWBERRY JUICE

Added Mg.	Found by titrimeter Mg.	Difference %
0.125	0.121	-3.2
0.250	0.252	+0.8
0.500	0.494	-1.2

### Summary and Conclusions

Because of the obvious difficulty in obtaining a rapid check on the use of the electrometric titrimeter to determine ascorbic acid in colored extracts, substances were studied with which it was possible to use the usual indophenol method. If a titration curve is drawn using the titrimeter, the values derived therefrom agree consistently with those of the ordinary visual titration. The indicating eye alone cannot be used, since the change in e. m. f. in the reaction is not rapid enough to cause a noticeable blink. Reducing substances, other than ascorbic acid, which are usually found in fruit juices, did not interfere with the end point.

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# Determination of Tetraethyllead in Gasoline

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Tetraethyllead in gasoline is determined quantitatively by refluxing the gasoline with concentrated hydrochloric acid, extracting the lead chloride with water, and determining the lead found by any of the standard methods.

AN EARLIER publication from this laboratory (1) described a method for the determination of tetraethyllead in gasoline, based on bromination of the gasoline and separation of the lead as bromide. This method has been in wide use since its publication, and appears to give satisfactory results in a majority of cases. It presents, however, certain difficulties when applied to highly cracked gasolines, on which results are apt to be low even if the operator is particularly skilled and careful, and it cannot be applied at all to such fuels as alcohol blends. These drawbacks, coupled with the recent demand for greater accuracy, have led to the development of an improved method which is described below. The principle of this method, treatment of the gasoline with concentrated hydrochloric acid, was first suggested by Ferreri (2) and has recently been proposed again by the Imperial Oil Company of Canada, in Sarnia, Ontario (3). The method described here is a modification of these earlier suggestions, aimed at an increase in rapidity and ease of handling without sacrifice of accuracy.

## Apparatus

The apparatus (Figure 1) is made of heat-resistant glass and consists of a 500-ml. boiling flask; a Hopkins reflux condenser, the vapor outlet of which is vented by a rubber tube to an outside vent or to a hood; a thistle tube of approximately 70-ml. volume with bead to indicate approximately 50 ml. of volume; a heating tube with a chimney for increasing convection in the liquid; a heating coil, 250 watts, made of 2.7 meters (9 feet) of No. 30 B. and S. Nichrome wire; and a rheostat of 25 ohms' resistance with a current carrying capacity of at least 2.0 amperes, for regulating the heater. (This apparatus is available through several makers of glassware and laboratory supply houses.)

## Method

The reaction consists in converting the tetraethyllead to lead chloride by refluxing the sample of gasoline with concen-

trated hydrochloric acid, and extracting the lead chloride with water, for determination by any standard method of analysis for lead.

## Procedure

Obtain the temperature of the sample of gasoline to be tested. If it is desired to follow the practice of the oil industry to refer measurements to the standard temperature of 60° F. (15.5° C.), the true tetraethyllead content of the gasoline at 15.5° C. is obtained by adding (subtracting) 0.1 per cent of the milliliters of tetraethyllead present for each degree Centigrade the temperature observed at the time of sampling the gasoline is above (below) 15.5° C.

Pipet into the flask, from a pipet calibrated for gasoline delivery, a 50-ml. sample of the gasoline to be tested, and add 50 ml. of heavy distillate [a straight-run petroleum distillate, of low acid heat and approximately 10 per cent distilled at 204° C. (400° F.) and 90 per cent at 238° C. (460° F.) (straight-run kerosene)] measuring it approximately by means of the bead or the thistle tube. Except in the case of benzene blends or gasolines of unusually low end point, equally satisfactory results may be obtained by omitting the heavy distillate and using 100 ml. of the sample. With highly volatile gasolines (75 per cent below 100° C.), omission of the distillate may lead to results which are low by 0.05 to 0.10 ml. of tetraethyllead per gallon of gasoline.

Add 50 ml. of concentrated hydrochloric acid (density 1.19) through the thistle tube, and then reflux the acid and gasoline. Use the full heat of the heater until boiling has begun (usually 0.5 to 1 minute), then by regulating the rheostat reduce the heat so that at no time a steady stream of condensate flows from the condenser. Reflux the gasoline and acid for 30 minutes, then turn off the heat. Hydrochloric acid fumes escape through the condenser, which must, therefore, be appropriately vented.

After a few minutes' wait to permit the acid and gasoline to cool, drain the acid into a 400-ml. beaker. Now add 50 ml. of distilled water through the thistle tube and reflux the water and gasoline for 5 minutes, using the full heat of the heater. Drain the water into the beaker containing the acid, and repeat the water extraction.

Evaporate the acid and water solution to dryness. To the dry lead chloride add 30 ml. of nitric acid and heat to oxidize any organic material which may be present. If one treatment with nitric acid is not sufficient to oxidize the organic material completely, repeat the oxidation until a white salt is obtained. Dissolve the dry lead salt in 10 ml. of dilute nitric acid, and determine the lead present in the solution by any standard procedure for lead.

(When the concentration of tetraethyllead is expressed in volume, the density of the pure material is taken as 1.65, which is equivalent to: 1 ml. of tetraethyllead = 1.0570 grams of lead.)

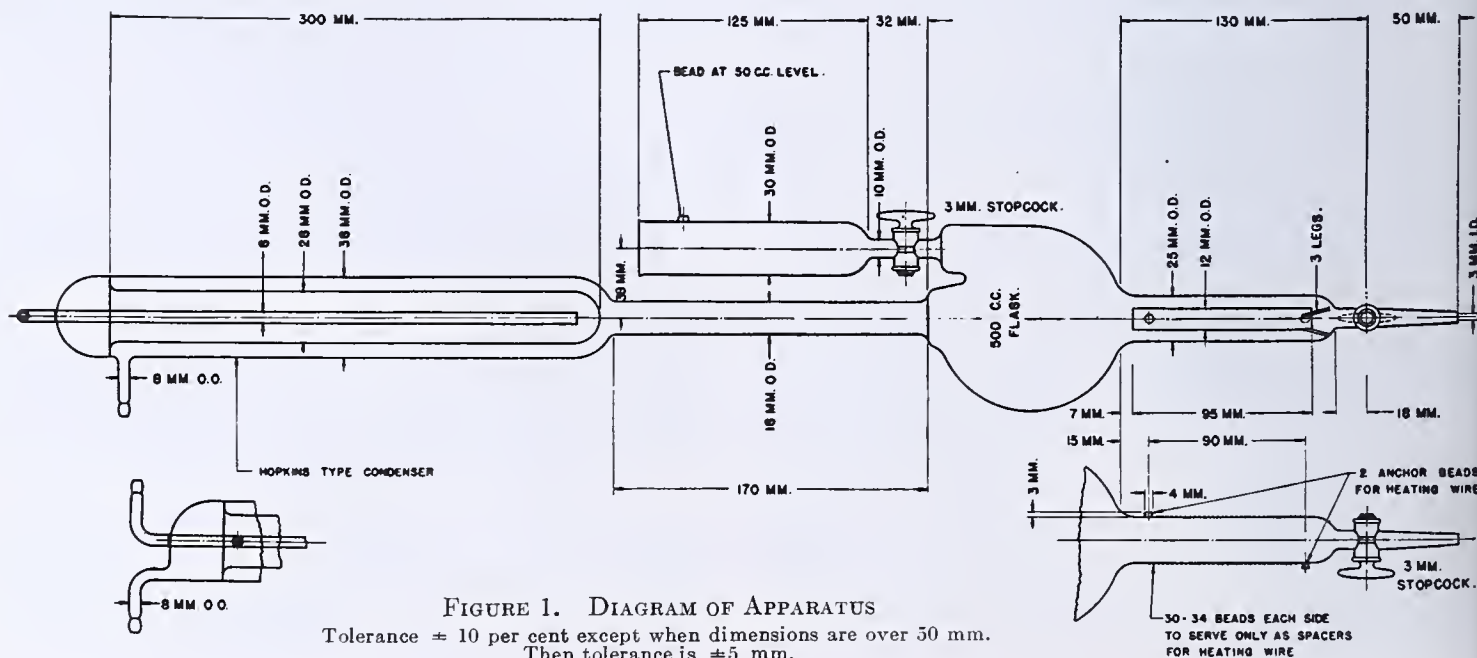


FIGURE 1. DIAGRAM OF APPARATUS

Tolerance = 10 per cent except when dimensions are over 50 mm. Then tolerance is  $\pm 5$  mm.



TABLE I. DETERMINATION OF TETRAETHYLLEAD IN GASOLINE

(Results in ml. of  $\text{Pb}(\text{C}_2\text{H}_5)_4$  per gallon at 15.5° C.)

Type of Gasoline:	Mean Error (Observed - Calculated)					Mean	Reliable Limits <sup>c</sup>	Precision <sup>d</sup>	
	Very volatile	Partly cracked			Highly cracked			Same laboratory	Different laboratories
Calculated Composition:	2.820	0.978	2.989	1.430	0.286	2.293	1.80	....	...
Regular <sup>a</sup> HCl reflux	-0.003 <sup>b</sup>	-0.010	-0.003 <sup>b</sup>	-0.011 <sup>b</sup>	-0.006 <sup>b</sup>	-0.039	-0.012	±0.006 <sup>c</sup>	0.026
No. of determinations	24	20	18	15	13	13			0.050
No. of laboratories	9	8	7	7	6	7			
Optional <sup>a</sup> HCl reflux	-0.028	-0.014	-0.019	-0.008 <sup>b</sup>	-0.005 <sup>b</sup>	-0.039	-0.019	±0.007 <sup>c</sup>	0.023
No. of determinations	28	32	42	33	31	34			0.032
No. of laboratories	12	13	14	14	14	13			
Bromine	-0.043	-0.013 <sup>b</sup>	-0.062	-0.041	-0.041	-0.124	-0.054	±0.011 <sup>c</sup>	0.075
No. of determinations	10	10	10	10	10	8			
No. of laboratories	6	6	6	6	6	5			

<sup>a</sup> Regular method, 50 cc. of sample + 50 cc. of heavy distillate. Optional method, 100 cc. of sample, no heavy distillate.<sup>b</sup> Error is not significant—i. e., does not differ reliably from zero.<sup>c</sup> Twice standard deviation of mean.<sup>d</sup> Twice standard deviation of individual results.<sup>e</sup> Depends upon care taken in bromination; one laboratory with extreme care obtained a precision of 0.012, three other laboratories with ordinary care obtained a precision of 0.062.

## Determination of the Lead

The lead present in the lead nitrate solution can be determined by any one of the regular standard procedures for lead. Satisfactory results have been consistently obtained in the laboratories of this corporation by the use of the methods described below.

**GRAVIMETRIC METHOD ( $\text{PbCrO}_4$ ).** Neutralize the nitric acid solution of the lead nitrate first with dilute ammonium hydroxide, adding 5-ml. excess, using *p*-nitrophenol or litmus as indicator, and then with dilute acetic acid, adding 1- to 2-ml. excess. Dilute the solution to 200 ml., and to the boiling solution add drop by drop 10 to 15 ml. of a 10 per cent solution of potassium dichromate. Boil the solution until a deep orange colored precipitate is obtained (10 to 15 minutes), cool, and allow to settle several hours or overnight. Collect the precipitate on a dried and weighed Gooch crucible, wash well with hot water, dry at 110° C., and weigh as  $\text{PbCrO}_4$ . (On an original sample of 50 ml. of gasoline, the weight of lead chromate multiplied by 48.533 will give the grams of lead per gallon of gasoline; multiplied by 915, it will give the milliliters of tetraethyllead per gallon of gasoline.)

**VOLUMETRIC METHOD ( $\text{PbMoO}_4$ ).** *Lead Nitrate.* Prepare a solution containing approximately 4.8 grams per liter of c. p. lead nitrate. Standardize the solution by precipitating the lead from an aliquot, as lead chromate, using the procedure described in the gravimetric method.

*Tannic Acid Indicator.* Prepare a 0.5 per cent solution in water of the U. S. P. fluffy tannic acid. This solution deteriorates on prolonged standing, and should be prepared at frequent intervals.

*Ammonium Molybdate.* Prepare a solution containing 2.38 grams per liter c. p. ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ . For standardization, take an aliquot of the standard lead nitrate solution, preferably 25 ml., make ammoniacal with dilute ammonium hydroxide to slight excess, and then make acid with dilute acetic acid, using 1- to 2-ml. excess. Dilute to 150 ml., and titrate hot with the ammonium molybdate solution, using tannic acid as an external indicator. (A small electric hot plate may conveniently be used, as the sample must be kept above 90° C. during the titration.) For the end-point tests care must be taken always to use the same amount of solution (4 drops) be added to the indicator solution (2 drops) contained in the depression of a spot plate. Determine a blank on the same amount of water and ammonium acetate, and subtract the amount of molybdate solution used (about 0.3 ml.) from the result of the titration.

The molybdate solution may be adjusted to be equivalent to 0.924 mg. of lead per milliliter, in which case 1 ml. of this solution added on an original 50-ml. sample of gasoline corresponds to 0.2 ml. of tetraethyllead per gallon of gasoline.

The concentration of lead nitrate solution may be adjusted to be equivalent to the molybdate solution, so that it may be used in adding known quantities of lead to the sample to complete the titration in case the sample is overtitrated.

*Procedure.* Determine the lead present in the nitric acid solution by the method described for the standardization of the ammonium molybdate solution.

For samples titrating, initially, less than 5 ml. of the molybdate solution, 10 ml. of the lead nitrate solution should be added before the titration is completed. The volume of the ammonium molybdate solution equivalent to the lead acetate solution is

subtracted from the titration volume before calculating the results.

## Discussion

The equipment and procedure as described above are the result of a fairly exhaustive investigation, and no obvious simplification of this method was found which would not sacrifice convenience, or accuracy, or both.

In addition to exhaustive tests in this laboratory on widely different types of gasolines, the method was tested by fourteen laboratories on 6 samples of gasoline made from 3 different base stocks. The results obtained are compared in Table I with the results obtained simultaneously by the bromination method (1).

Comparing the three methods, it will be observed that the mean errors for the hydrochloric acid reflux methods are considerably less than for the bromine method. This corresponds to a more complete lead recovery by the hydrochloric acid reflux methods. The regular hydrochloric acid reflux method has less mean error than the optional method.

The precision, which is a measure of how closely results check each other, is approximately equal for results obtained in the same laboratory by either the regular or optional hydrochloric acid reflux methods. When comparing results obtained in different laboratories, the precision is somewhat better for the optional method than for the regular method and both are considerably better than the bromine method. The superiority of the optional method in this respect, which is under consideration only when comparing a result obtained in one laboratory with a result obtained in another laboratory, is ascribed to the variations in technique and burets in different laboratories. The titration error introduced by such variations has a higher relative effect in the regular method because the sample is only half as large as in the optional method.

## Conclusions

Table I indicates that the new method yields results with a mean error of only -0.012 ml. of tetraethyllead per gallon of gasoline, as against -0.054 for the bromination method, the improvement being particularly noticeable in the case of cracked gasolines. Furthermore, the precision of the new method is greater than for the bromine method, the upper limit for the variation between laboratories being 0.050 ml. of tetraethyllead per gallon of gasoline by the new method, as compared with 0.075 by the bromine method.

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# Separation of Cobalt from Manganese

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THE quantitative separation of cobalt from manganese by any known method is difficult. Manganese dioxide precipitated by potassium chlorate and nitric acid tends to carry down some cobalt with it. Precipitation of cobalt sulfide in acetic acid solution does not always give a sharp separation; either some manganese remains with the cobalt or some cobalt with the manganese, or both. The separation here proposed has been suggested by Prescott and Johnson (5) and by Lundell and Hoffman (3), but no figures to show its accuracy have been published. The usual procedure of separating cobalt from manganese as potassium cobaltinitrite appears somewhat longer than the proposed method, as it requires the removal of ammonium salts and is intended for a few milligrams of cobalt only.

Although cobalt phosphate by itself is soluble in ammonia in the presence of manganese both metals are quantitatively precipitated by ammonium phosphate unless citrate ions are present. As little as 2 mg. of cobalt can be quantitatively separated from 0.1 gram of manganese after the addition of 2 grams of citric acid, when the phosphate precipitation is made by the method of W. Gibbs (1, 2), in which manganese phosphate is slowly precipitated at boiling temperature by the addition of dilute ammonia. The concentration of manganese should not exceed 0.1 gram of manganese in 100 ml. containing 1 to 2 grams of ammonium phosphate and 20 grams of ammonium chloride.

Ammonium citrate appears to act as a differential retarding agent by permitting only a partial retention of cobalt, while only slightly retarding the precipitation of manganese. This permits a fairly clean-cut separation of the two metals in from one to three precipitations of manganese phosphate. The color of the precipitate is helpful in judging the extent of separation. Pure manganese phosphate, which is flesh-colored, becomes lilac in the presence of 1 mg. or more of cobalt.

It is permissible to determine cobalt quantitatively as the sulfate, which may be dehydrated at 600° C. without dissociation (4). Consistently accurate results were obtained with quantities up to 0.4440 gram of cobalt sulfate. It is advisable to re-ignite the sulfate as a check for constant weight without an intervening evaporation with water and to stir it with a platinum wire before ignition. This avoids decrepitation and gives the same final weight of cobalt sulfate as that obtained by evaporation with water. No manganese was found in the cobalt sulfate by the colorimetric test.

Any cobalt retained by the manganese phosphate is conveniently determined colorimetrically as the blue cobalt chloride (6). The slight green color of cobalt blue, which is perhaps due to iron or some other slight impurity, may be partly overcome by reduction with a little sodium sulfite.

## Reagents and Solutions

**COBALT NITRATE SOLUTION.** Filter a concentrated solution of the c. p. crystals in hot water, add an equal volume of concentrated nitric acid, and allow the cobalt nitrate to crystallize out overnight. Use the wet crystals to prepare a stock solution containing 1 mg. of cobalt per milliliter. The actual strength was established by evaporating 30 ml. with 2 drops of 1 to 1 sulfuric acid and igniting the residue at 600° C.

**CITRIC ACID SOLUTION.** Dissolve 20 grams of the crystals in 100 ml. of water.

**AMMONIUM PHOSPHATE.** Use the solid diammonium reagent.

**AMMONIUM CHLORIDE.** Use the solid reagent.

**MANGANESE SULFATE SOLUTION.** Use c. p. manganese dioxide to prepare a solution containing 10 mg. of manganese per milliliter.

## Procedure

The solution of cobalt and manganese, which has been freed from other members of the ammonium sulfide group as well as the alkaline earths, may be the filtrate from the basic acetate precipitate if only minor quantities of calcium and magnesium are present. More than a few milligrams of the alkaline earths are undesirable because of their pronounced retentive action on cobalt when a group precipitation of phosphates is made. Magnesium phosphate has a remarkable high adsorptive power and is particularly objectionable.

\* The solution is treated by the Gibbs method for the precipitation of manganese phosphate, except that it also contains 2 grams of citric acid in each 125 ml. The precipitation should proceed slowly. The final precipitate of manganese phosphate is filtered off and washed twice with very dilute ammonia and dissolved in just enough 1 to 1 hydrochloric acid. This solution is caught in the precipitation beaker and evaporated to dryness on the steam bath. For the colorimetric determination of cobalt, the residue is dissolved in 20 ml. of 1 to 1 hydrochloric acid and transferred to a porcelain crucible of 30-ml. capacity, reduced with a few crystals of sodium sulfite, and heated on the steam bath till the volume is about 10 ml. A series of standards from 0.3 to 1 mg. of cobalt at 0.3 mg. intervals is similarly treated on the steam bath. From it the quantity of cobalt in the manganese phosphate may be closely determined.

The combined filtrates from the manganese phosphate are concentrated to a volume of 200 to 300 ml. Bromocresol purple is added until the cobalt solution is decidedly colored, and it is then made slightly acid with 50 per cent acetic acid, or to the complete disappearance of the purple color at pH 5.2. Precipitation of cobalt sulfide will be complete at this acidity. It is saturated with hydrogen sulfide in an Erlenmeyer flask of suitable size, provided with the usual inlet and outlet tubes; then the tubes are closed and the flask is heated to about 70° C. on the steam bath until the cobalt sulfide coagulates, about one hour.

The filtered and washed cobalt sulfide is dried and ignited slowly in a 30-ml. porcelain crucible. After all carbon is gone the cobalt oxide is dissolved in just enough 1 to 1 hydrochloric acid and evaporated to dryness. The precipitation flask is cleaned with a little hot 1 to 1 nitric acid which is added to the cobalt chloride in the crucible, together with 2 to 8 drops of 1 to 1 sulfuric acid—the latter quantity for 0.2 gram of cobalt. When all liquid is evaporated, the crucible is slowly heated in a radiator until the excess of sulfuric acid is apparently gone. The bottom of the crucible is then heated directly in the Bunsen flame to dull red for about one minute. The ignition at 550° to 600° should be repeated until the cobalt sulfate reaches constant weight.

The experimental results appear in Table I.

Experiments 1 to 7, which cover a range from 2 to 1 mg. of cobalt, show that the quantitative separation of cobalt and manganese phosphates in the presence of ammonium c

TABLE I. DETERMINATION OF COBALT IN THE PRESENCE OF MANGANESE

Expt.	Taken				Cobalt Found in Phosphate Precipitate	Cobalt as CoSO <sub>4</sub>	Total Cobalt Found	Error
	Co	Mn	Ca	Mg				
	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram
1	0.0021	0.1000	....	....	0.0000 <sup>a</sup>	0.0021	0.0021	0.00
2	0.0060	0.1000	....	....	0.0005	0.0058	0.0063	+0.00
3	0.0123	0.1000	....	....	0.0008	0.0114	0.0122	-0.00
4	0.0249	0.1000	....	....	0.0003	0.0254	0.0257	+0.00
5	0.0562	0.1000	....	....	0.0001	0.0560	0.0561	-0.00
6	0.1045	0.1000	....	....	0.0006	0.1043	0.1049	+0.00
7	0.1687	0.2500	....	....	0.0006 <sup>b</sup>	0.1676	0.1682	-0.00
8	0.0509	0.2500	0.1000	....	0.0003	0.0518	0.0521	+0.00
9	0.0509	0.2000	0.0400	0.0400	0.0024	0.0497	0.0521	+0.00
10	0.0509	0.1000	....	0.0400	0.0008 <sup>b</sup>	0.0511	0.0519	+0.00

<sup>a</sup> One precipitation.

<sup>b</sup> Three precipitations.



is fairly satisfactory. Experiments 8 to 10 show the reverse effect of the alkaline earths, which are not precipitated as completely as manganese phosphate and tend to accompany cobalt sulfide. An electrolytic determination of cobalt would be better in such cases.

If the alkaline earths are likely to be present in only very minor quantities, they may be precipitated jointly with manganese phosphate. This step shortens the procedure by avoiding the previous separation of cobalt and manganese with ammonium sulfide. The presence of an appreciable quantity of magnesium is strongly suggested by the deepened color of the first phosphate precipitate. In such case, the precipitate should be dissolved in just enough hydrochloric acid, the quantity of citric acid doubled to 4 grams in 125 ml., and the precipitation repeated. Three precipitations would be sufficient in any case.

This procedure, which is reasonably rapid, is especially adaptable to the analysis of cobalt-bearing psilomelane, which is very high in manganese and low in alkaline earths. The manganese in the phosphate precipitate may be readily

determined by the bismuthate method, if it contains only a negligible quantity of cobalt.

By igniting cobalt sulfate at 550° to 600° C. all free acid may be safely expelled, thus permitting a rapid determination and the handling of larger quantities than have been thought advisable heretofore. The ignited sulfate is completely soluble in cold water.

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# Warder's Method for the Titration of Carbonates

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A critical survey of Warder's method and of the literature pertaining to it shows that titration of carbonate to bicarbonate must be performed in a closed system to avoid loss or gain of carbon dioxide. A titration procedure which is essentially identical with that of Tillmans and Heublin is described in detail so as to assure acceptable results. Its accuracy and precision have been tested on a carbonate-bicarbonate solution having a carbon dioxide tension of approximately 0.0003 atmosphere so as to render the solution reasonably stable in contact with air.

The relative average deviation of the titration of carbonate to bicarbonate has been found approximately equal to 1.5 parts per thousand. The de-

termination of the titratable base can be performed with a precision of 0.5 part per thousand. Calculations based on these figures show that in the application of Warder's method to the determination of hydroxide, carbonate, and bicarbonate in the presence of one another the precision becomes poor whenever the mass of the constituent determined is less than one tenth of the mass of the major component. Traces of carbonate in hydroxide may be determined by the use of a refined titration technique, but it would be hopeless to attempt with Warder's method the determination of traces of hydroxide in carbonate, traces of carbonate in bicarbonate, or traces of bicarbonate in carbonate.

A SURVEY of the literature on Warder's method (42) reveals great differences in the performance of the titration (6, 12, 17, 22, 27, 30, 31, 36, 37, 39), and the reliability of the method appears a matter of controversy. Theoretical analysis of the problem permitted an adequate evaluation of individual publications, but an experimental investigation seemed necessary for the confirmation of the conclusions. A review of the literature at the close of the investigation finally showed that, while all the required precautions were known, not one of the authors customarily considered had succeeded in describing an entirely satisfactory procedure.

The principal aspects of the titration of carbonates may be derived from Figure 1, in which it is assumed that 10-ml. portions of sodium carbonate solutions are titrated with standard acids of the same molar concentrations as the carbonate solutions. pH curves I, II, and III have been calculated for 1 molar, 0.1 molar, and 0.01 molar solutions, respectively. The pH at the bicarbonate equivalence point is

the same for all concentrations (28), while the pH at the carbon dioxide equivalence point varies considerably with changes of the concentration. The curves through  $E_1$  and  $E_3$  show the continuous change of the carbon dioxide tension of the titrated solutions. The carbon dioxide tension has been calculated as a function of the hydrogen-ion concentration (11) and the sodium-ion concentration by means of the equation

$$P_{\text{CO}_2} = 8.2 \times 10^7 [\text{H}^+] \frac{[\text{H}^+]^2 + [\text{H}^+] [\text{Na}^+] - 10^{-14}}{7.8 \times 10^{-11} + [\text{H}^+]} \text{atmosphere}$$

The common logarithms of the carbon dioxide tensions have been plotted against the volumes of standard acid added. The horizontal line  $E_1E_3$  indicates the tension 0.0003 atmosphere, which corresponds to the partial pressure of carbon dioxide in air containing 0.03 per cent by volume of this gas. The curves, through  $E_1$  for molar solutions and through  $E_3$  for 0.01 molar solutions, show clearly that the titrated solu-



tions are in general not in equilibrium with the atmosphere (7, 11, 24, 39).

### Carbon Dioxide Tension and Performance of Titration

It is obvious that production of correct results with Warder's method requires that the carbon dioxide content of the titrated material be kept constant until the bicarbonate end point is adjusted (24); losses or gains of significant quantities of carbon dioxide must be prevented.

The slow rate of hydration in the interval from pH 11 to 8 determines the conditions which actually prevail during titration to the bicarbonate end point. The addition of every portion of standard acid creates in the titrated solution locally, close to the surface, a strongly acid region containing a high concentration of carbonic acid which immediately dehydrates to carbon dioxide. Considerable losses of carbon dioxide are imminent at this stage, and quick dissipation of the acid region by mixing gives no radical improvement, since considerable time is required until the carbon dioxide

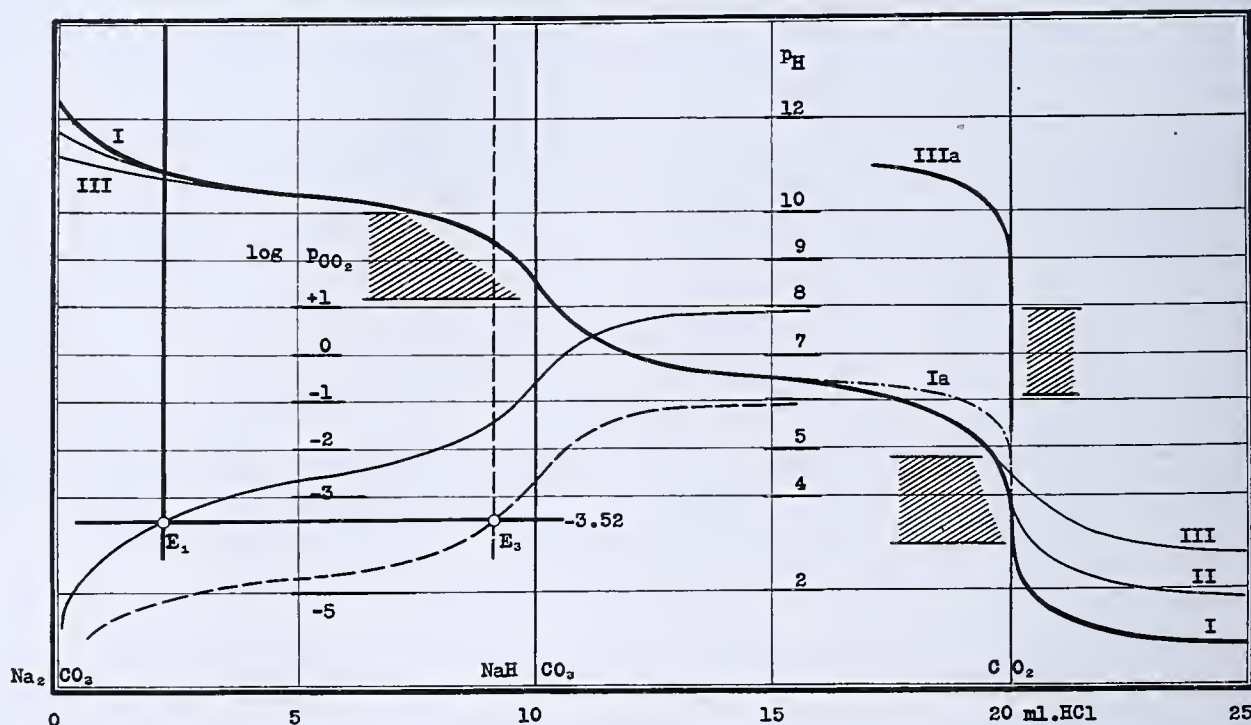


FIGURE 1. TITRATION OF CARBONATES

The instability of solutions of carbonate and bicarbonate in contact with air is shown by Figure 1. At the bicarbonate equivalence point the carbon dioxide tension exceeds 0.1 atmosphere with molar solutions and 0.001 atmosphere with 0.01 molar solutions (11, 21, 39). It is true that bicarbonate solutions lose carbon dioxide very slowly when standing in contact with air, but the rate of loss is greatly increased by the mixing operations which are necessary during titrations. Losses averaging 9 per cent of the carbon dioxide present were observed with 0.1 molar and 0.01 molar solutions of pure sodium carbonate decahydrate when, in the authors' experiments, titrations were carried out at freezing temperature in open 250-ml. Erlenmeyer flasks. The occurrence of losses of such magnitude is explained by the fact that, during titration, the carbon dioxide tensions for most of the time exceed those shown in Figure 1, which have been calculated for conditions of equilibrium.

The rate of hydration of carbon dioxide is far lower than the rate of dehydration of the carbonic acid, and even dilute solutions of carbon dioxide contain approximately 99 per cent anhydride ( $\text{CO}_2$ ), 0.9 per cent bicarbonate ion, and only 0.1 per cent carbonic acid ( $\text{H}_2\text{CO}_3$ ) (5, 35). Thiel (34), Faurholt (5), and Brinkman, Margaria, and Roughton (4) came to the conclusion that in alkaline solutions the reaction  $\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$  prevails, the rate obviously depending upon the hydroxyl-ion concentration. The times required for approach within 10 per cent of equilibrium are given as follows (5):

At pH 14 to 12, a small fraction of a second  
At pH 12 to 11 and 4 to 0, a few tenths of a second  
At pH 11 to 10 and 6 to 4, 1 to 10 seconds  
At pH 8, 80 seconds

bound by reaction with the hydroxyl ion of the weakly alkaline solution. Efficient stirring, which would prevent the temporary formation of strongly acid regions, is not admissible, for it would greatly facilitate the exchange of carbon dioxide between solution and atmosphere.

The necessity of avoiding loss of carbon dioxide was recognized from the very beginning. Warder himself (42) recommended titration of dilute solutions, a provision which is not sufficient, however, for the titration of mixtures of carbonate and bicarbonate. Thomson (36) recommended in 1883 "keeping the point of the buret in the liquid, so that no carbonic acid escapes." The buret was used "with a long capillary spit reaching nearly to the bottom of a tall narrow cylinder in which the liquid was titrated with continual stirring by a circular glass rod, which was never lifted above the surface of the liquid" (29, 30). Kippenberg (12) seems to have been the first to recommend performance of the titration in a stoppered flask (7, 11, 37, 39).

### Adjustment of Bicarbonate End Point

The adjustment of the bicarbonate end point requires (1) the use of a color standard for the adjustment of the end point (3, 23), and (2) allowance of sufficient time after each addition of standard solution for the establishment of equilibrium. The slow hydration of carbon dioxide, which is responsible for the "fading of the phenolphthalein color" (20, 40), has been discussed.

The color standard for the adjustment of the end point which is easily prepared with the use of pure bicarbonate must be protected against loss of carbon dioxide and, for obvious reasons, is kept in a stoppered flask of the type used in the titrations. The color standard must contain the same quantity of indicator as the titrated solution, and it must



approximate the solution which has been titrated to the bicarbonate end point with respect to volume, bicarbonate concentration, total ion concentration, and temperature (2, 14).

Phenolphthalein is recommended for the indicator; thymol blue (27) appeared definitely less satisfactory. Excellent results were obtained with Simpson's indicator (31), but its usefulness may be expected to show great variations, depending upon the ability of the experimenters to match shades of orange. The use of a one-color indicator, such as phenolphthalein, requires special attention to the selection of the proper indicator concentration. The intensity of coloration produced by such indicators in a solution of a definite concentration is directly proportional to the stoichiometric concentration of the indicators (1). Thus, it is absolutely necessary to add equal masses of indicator to the titrated solution and color standard. As a matter of common sense, the quantity of indicator is chosen so as to produce a tint permitting precise colorimetric matching (22).

The coloration produced by phenolphthalein in a bicarbonate solution depends on the total ion concentration and the temperature of the solution (10, 14). Cooling and addition of neutral salts were used (17) in order to obtain a "colorless" solution at the phenolphthalein end point. The shape of the pH curve makes it impossible, however, to obtain an abrupt change of color, and adjustment to a definite shade of "colorless" is, of course, far more difficult than the reproduction of a pink which has been intentionally chosen because of its suitability for colorimetric matching. Comparison of the "colorless" solution with a sample of water reveals the definitely pink hue of the former.

### Adjustment of Carbon Dioxide End Point

The procedure for the adjustment of the carbon dioxide end point must depend essentially upon the concentration of the titrated solution (Figure 1). Tenth molar and stronger carbonate solutions are best titrated with the use of bromophenol blue to a greenish gray coloration, pH 4, taking care to remove from the titrated solution by agitation as much carbon dioxide as possible. More dilute carbonate solutions are best treated with a slight excess of standard acid, boiled to remove the liberated carbon dioxide, cooled to room temperature, and then titrated back with standard alkali, using an indicator acting at approximately pH 7. The attainment of an end point close to pH 7 is essential for precise determinations of the titratable base of very dilute solutions. In the back-titration the pH of the solution follows the steep curve, IIIa, of Figure 1 and, around pH 7, a small volume of standard solution is able to change the color of the indicator. Curve III for the titration in the presence of carbon dioxide indicates low precision of the adjustment of the end point and the necessity of using a color standard.

The suitability of the proposed procedures may be derived from the results of the following experiments. Eleven 50-ml. portions of an approximately 0.1 molar solution of pure sodium carbonate decahydrate were titrated with 0.5 molar standard acid, using bromophenol blue as indicator. As the arithmetical mean of 11 determinations,  $21.53 \pm 0.01$  ml. of acid were required for the neutralization of the titratable base. Then the 0.5 molar standard solutions and the 0.1 molar carbonate solution were diluted ten times, using the same volumetric apparatus in the titration of all the solutions. Fifty-milliliter portions of the 0.01 molar sodium carbonate solution obtained were now titrated with the use of 0.05 molar standard acid and standard alkali. The carbon dioxide was eliminated by boiling and bromothymol blue was used as indicator for the back-titration to pH 7. As the mean of 7 titrations  $21.53 \pm 0.02$  ml. of the 0.05 molar acid were required, which is in satisfactory agreement with the result of the former series of determinations.

The traditional use of methyl orange (17, 42) offers no decided disadvantages in the titration of strong carbonate solu-

tions. The change of color occurs in the pH range between 4.8 (yellow) and 3.0 (red). Curve I of Figure 1 indicates that with 1 molar solutions the color will gradually change before the equivalence point is reached. Beyond that point, one drop of standard acid will suffice to change the color from orange to red, and the appearance of red should, therefore, be chosen as end point. In the calculation of curves I, II, and III it was assumed that no carbon dioxide is given off during the titration. If care is taken, however, to eliminate by agitation most of the carbon dioxide formed, the pH of the solution will approximately follow curve Ia, and a far more sharply defined change of the color of methyl orange will be obtained at the end point.

Reinitzer (26) was probably the first to recognize the influence of carbon dioxide on the color of methyl orange, but even today there seem to be differences of opinion concerning the suitability of this indicator. From Figure 1 it is obvious that methyl orange can be employed for the titration of approximately 0.1 molar and stronger carbonate solutions, especially if a color standard is used (3, 15, 17, 23). The titration of 0.01 molar or even 0.001 molar carbonate solutions with the use of methyl orange should not be attempted; it must be kept in mind that 100 ml. of distilled water need 1 ml. of 0.01 molar acid and more than 10 ml. of 0.001 molar acid to acquire a pH of 4 (3).

### Procedure

The titration is carried out in a 250-ml. volumetric flask with long narrow neck and glass or cork stopper (37). Two more flasks of the same size, shape, and make are needed; one holds the color standard, the other is filled with plain water.

Of solid materials and strongly alkaline solutions, an amount that will require approximately 40 ml. of 0.5 *N* acid to neutralize all the titratable base is transferred into the volumetric flask and treated with 50 ml. of distilled water which has been freed from carbon dioxide. If the sample contains large or moderately large quantities of carbonate, the distilled water may be "freed" from carbon dioxide by shaking it in a large flask while suction is applied. Special precautions (9) are required for the determination of traces of carbonate. For the titration of dilute alkaline solutions it is advisable to use standard acid of such normality that approximately 10 ml. are required for neutralization of the titratable base of 80 ml. of sample.

The color standard for the bicarbonate equivalence point must resemble the titrated solution at this point in volume, bicarbonate concentration, total ion concentration, and temperature; furthermore, it must contain the same mass of indicator as the titrated solution. Obviously, an approximate knowledge of the composition of the sample is required.

Some U. S. P. sodium bicarbonate is stirred for about 3 minutes with distilled water. The mixture is transferred to a Büchner funnel, strong suction is applied, and the cake of salt is washed once with cold distilled water. When the bicarbonate begins to dry, the required quantity of the still slightly moist salt is weighed out on a horn-pan balance and transferred to the volumetric flask. The calculated quantity of neutral salt and distilled water, previously freed from carbon dioxide, are added. The flask is immediately stoppered and then shaken until all solids have dissolved. Finally, a 1 per cent solution of phenolphthalein in alcohol is added from a medicine dropper or graduated pipet until the solution assumes a pink coloration. Approximately 0.1 ml. of the indicator solution will produce a tint satisfactory for colorimetric matching.

Exactly the same amount of phenolphthalein, as used in the preparation of the color standard, is added to the solution to be titrated. The titrated solution and the color standard are always kept stoppered. The flask containing the titrated solution is opened only for the addition of standard solution and then im-



mediately closed again. At the start of the titration, the standard acid is added in relatively large portions and, after every addition, the contents of the flask are vigorously shaken for about 20 seconds so as to establish equilibrium between the gaseous and the liquid phases. When the color of the titrated solution has brightened to pink, the standard acid is added in portions of 0.2 ml., single drops, and eventually fractions of drops. Simultaneously the time of shaking is the more prolonged the nearer the titration approaches the end point. When this point seems to have been reached, it becomes necessary to shake one full minute and to wait another minute before comparing with the color standard. It is advisable to shake the color standard just as often and as long as the titrated solution, to make certain that the equilibrium with the gaseous phase is established in the standard also. For the close matching of colors it is convenient to place the flasks on a large sheet of white paper. The flask with plain water will be found helpful when comparing the pink solutions. Strongly colored solutions cause fatigue of the eyes and must be kept away from the titration table.

For the titration to the carbon dioxide end point the stopper is removed and rinsed off into the titrated solution with 10 or 15 drops of distilled water. After addition of the proper indicator, the titration is continued, shaking the solution from time to time to accelerate the escape of carbon dioxide. The choice of indicator and procedure for the adjustment of the end point have been discussed above. The use of standard alkali is permissible in the adjustment of both end points.

TABLE I. TITRATION OF TEST SOLUTIONS

		Na <sub>2</sub> CO <sub>3</sub> G./l.	NaHCO <sub>3</sub> G./l.
Solution I	Calculation	12.715 ± 0.0032	13.446 ± 0.0027
	Warder's method	12.78 ± 0.013	13.38 ± 0.019
	Winkler's method	.....	12.97 ± 0.017
Solution II	Calculation	12.708 ± 0.0051	13.445 ± 0.0027
	Warder's method	12.60 ± 0.023	13.63 ± 0.034
	Winkler's method	.....	13.38 ± 0.0083

### Accuracy of the Suggested Procedure

The test material was a solution that contained known quantities of carbonate and bicarbonate in such proportion that the carbon dioxide tension of the solution approximated the partial pressure of carbon dioxide in the atmosphere. Thus it was hoped to overcome the difficulties arising from the variation of composition due to the exchange of carbon dioxide between liquid and air. Since the reliability of simple procedures for the preparation of pure sodium bicarbonate and pure sodium carbonate could be subject to controversy (18, 19, 32, 41), it was decided to base all calculations on the analyses of these substances.

U. S. P. sodium bicarbonate was repeatedly washed with water and quickly dried. The salt thus purified was free from ammonium, chloride, and sulfate ions, as could be demonstrated by qualitative tests. Part of this bicarbonate was used for the preparation of anhydrous carbonate. Use of a platinum crucible and heating in a Stähler block eliminated the possibility of contamination by combustion products of the Bunsen flame.

**STANDARD ACID AND ALKALI.** The 0.5 *N* standard solutions were prepared and kept in 7-liter stock bottles which were permanently connected with the calibrated burets. An arrangement of washers and soda-lime tubes, similar to that employed by Lindner (18), prevented changes of the standard solutions by either evaporation of water or absorption of carbon dioxide. The stock bottles were filled with distilled water and then, using a gas diffuser stone of cylindrical form, air free from carbon dioxide was bubbled through the water for 7 hours. After this treatment for the removal of carbon dioxide the calculated amounts of hydrochloric acid and oily lye, respectively, were added, the bottles were closed, and the contents were mixed by shaking. Finally, the stock bottles were permanently connected to the burets.

For the determination of the titer, 25 ml. of the acid were measured with the buret and precipitated with silver nitrate. The weight of the silver chloride was corrected for the buoyant effect. As the arithmetical mean of three determinations, 0.48695 ± 0.00007 (±0.14%) gram-equivalent weight per liter was found

for the normality of the acid. The titer of the standard alkali was determined at short intervals by titration with the standard acid. All titrations were carried out at a temperature of approximately 25° C.; on very few occasions did it deviate from this norm as much as ±4° C. With the temperature nearly constant and the solutions always dispensed by the same burets, any errors caused by the use of the 0.5 *N* standard solutions are automatically eliminated.

**TITRATION OF PURIFIED SODIUM BICARBONATE.** The determination of the bicarbonate content was tried by weighing the carbon dioxide obtained on decomposition. In one series of experiments carbon dioxide and water were liberated by heating the bicarbonate at 290° C. in a combustion tube; in the other series, the bicarbonate was decomposed with dilute acid. The precisions of both methods proved inadequate for the establishment of the degree of purity of sodium bicarbonate, and it was finally decided to measure the total alkalinity, which can be determined with high precision.

Five 1.4- to 1.8-gram portions of bicarbonate were titrated using methyl red as indicator. An excess of acid was added first and the carbon dioxide was removed by boiling for 2 minutes. After cooling to room temperature the end point was adjusted by titrating with standard alkali to yellow. The weight of the sodium bicarbonate was corrected for the buoyant effect. In determinations 24.443 ± 0.003 (±0.12%) ml. of standard acid were required for the titration of 1.00000 gram of bicarbonate. From this figure the bicarbonate content was calculated (2) 100.00 ± 0.02% NaHCO<sub>3</sub>. The presence of 0.1 per cent of sodium carbonate in the bicarbonate would increase the above value by 0.06 per cent.

**TITRATION OF SODIUM CARBONATE.** Three 1-gram portions of the sodium carbonate were titrated with standard acid and alkali using the same procedure as in the determination of the titrated base in sodium bicarbonate. The weight of the sodium carbonate was corrected for the buoyant effect. In 3 titrations 38.718 ± 0.008 (±0.2%) ml. of standard acid were required per 1.000 gram of carbonate. Calculation gives a content of 99.93 ± 0.024% Na<sub>2</sub>CO<sub>3</sub>.

**PREPARATION OF TEST SOLUTIONS.** Approximately 160 millimoles of sodium bicarbonate and 120 millimoles of sodium carbonate were dissolved to 1 liter of solution. The distilled water was boiled beforehand to expel the carbon dioxide dissolved; for cooling the water to room temperature the flask was closed with a stopper carrying a soda-lime tube. The following quantities of salts were taken for the preparation of 1.00000 liter of test solution:

Test solution I	13.4461 grams of NaHCO <sub>3</sub>
	12.7236 grams of Na <sub>2</sub> CO <sub>3</sub>
Test solution II	13.4450 grams of NaHCO <sub>3</sub>
	12.7236 grams of Na <sub>2</sub> CO <sub>3</sub> (99.88%)

All weights were corrected for the buoyant effect, and the solutions were kept in stoppered flasks.

**TITRATION OF TEST SOLUTIONS.** All these titrations were carried out in 250-ml. volumetric flasks with long narrow necks, and for each experiment a 49.967 ± 0.0015-ml. portion of test solution was taken. During the titrations the scale of the acid buret was kept covered so as to eliminate bias in the adjustment of the end points.

In 10 titrations of test solution I, using the suggested procedure for the performance of Warder's method the following volumes of standard acid were required:

12.38 ± 0.011 (±0.9%) ml., bicarbonate end point
41.100 ± 0.0057 (±0.14%) ml., carbon dioxide end point

These 10 titrations were carried out within 7 days from the preparation of the test solution. Twelve days later this solution was titrated, using Winkler's method (43) as described by Kihoff and Sandell (16), but employing strontium chloride in the place of barium chloride for the precipitation of carbonate. In 4 titrations the volumes of sodium hydroxide standard solution required for the conversion of the bicarbonate to carbonate corresponded to 15.84 ± 0.02 (±1.3%) ml. of the standard acid.

Since the time interval between the two series of titrations was obviously too long, another series of experiments was started and all the titrations were carried out within 3 days from the preparation of test solution II. In 5 determinations using Warder's method the following volumes of standard acid were required:

12.20 ± 0.02 (±1.75%) ml., bicarbonate end point
41.056 ± 0.006 (±0.14%) ml., carbon dioxide end point



n 4 titrations with the use of Winkler's method, a volume of hydroxide solution was required which was equivalent to  $16.345 \pm 1$  ( $\pm 0.62\%$ ) ml. of the standard acid.

The results of the titrations are compiled in Table I. As indicated by the average deviations of the means, the significance of the deviations between experiment and calculation in general, doubtful. The deviations of the values for carbonate and bicarbonate obtained with Warder's method are probably of an accidental nature, and it appears that the method is able to give correct results (33). The limitations spring from its lack of precision as outlined below.

The results obtained with Winkler's method deviate significantly from the calculated values. As already mentioned, the error 12.97 is explained by loss of carbon dioxide while test solution I was standing for 12 days. It is obvious that carbonate-bicarbonate solutions can be stable only at a definite temperature and contact with air of a definite carbon dioxide pressure. Actually neither of these factors was under control.

### Precision of Warder's Method

The following calculations are based upon the assumption that sodium salts are titrated, but substitution of the proper equivalent weights in the final equations permits their application to other carbonates and hydroxides. Titration to phenolphthalein end point and the determination of the titratable base allow calculation of the hydroxide, carbonate, bicarbonate, and total carbonic acid. Bicarbonate-carbonic acid mixtures are not considered here, and it is understood that hydroxide and bicarbonate cannot occur simultaneously.

THE TITRATABLE BASE,  $P_{Na}$ , is calculated as a function of volume,  $M$ , of standard acid required to reach the carbon dioxide end point. If  $S$  represents the amount of sample,  $N$  normality of the standard acid, and 2.3 one tenth of the equivalent weight of the constituent determined, the exact relation between  $P_{Na}$  and  $M$  is given by

$$P_{Na} = \frac{2.3 NM}{S}$$

The precision of the determination of titratable base depends mainly upon the precision,  $\mu$ , of  $M$ —i. e., on the precision of the adjustment of the carbon dioxide end point. The relative average deviation,  $\mu'$ , of a single observation should not exceed  $0.5\%$ , if proper care is exercised and proper judgment is used in the selection of buret and concentration of the standard solution. In the two series of titrations listed in the preceding section,  $\mu'$  was found equal to  $\pm 0.45\%$  (10 determinations) and  $\pm 0.32\%$  (5 determinations), respectively. With the use of special precautions (8, 9) the precision of  $M$  may be considerably improved, but  $\mu' = \pm 0.5\%$  should be considered a fair figure, if a standard procedure of titration is used. It follows (2) that the relative average deviation,  $\pi'_{Na}$ , of a single determination of the content  $P_{Na}$  of titratable base is

$$\pi'_{Na} = \mu' = 1000 \frac{\mu}{M} = \pm 5\% \quad (1)$$

From the above two equations are derived the following relations which are needed later:

$$\mu = \pm \frac{M}{2000} \quad (2)$$

$$M = \frac{SP_{Na}}{2.3 N} \quad (3)$$

THE TOTAL CARBONIC ACID is always a direct function of  $M_1 = M_2$ , the volume of standard acid required for the

titration from the bicarbonate end point to the carbon dioxide end point:

$$P_{CO_2} = \frac{4.4 NM_2}{S} \quad (4)$$

This relation holds for mixtures of hydroxide and carbonate and for mixtures of carbonate and bicarbonate. Thus, the equation

$$M_2 = \frac{SP_{CO_2}}{4.4 N} \quad (5)$$

is valid for the whole of the following discussion.

The precision of the result for total carbon dioxide obviously must depend upon precision  $\mu_1$  of  $M_1$  as well as on precision  $\mu$  of  $M$ . In other words, the precision of the determined content of carbon dioxide will depend upon the precisions of the adjustments of the bicarbonate end point and the carbon dioxide end point. The latter precision is a function of the amount of titratable base present, as shown in Equation 2. The absolute precision of the adjustment of the phenolphthalein end point depends altogether on the amount of bicarbonate present at this stage of the titration and is the same as obtained in the titration of an equivalent quantity of carbon dioxide with the use of standard alkali (13, 38). It has been demonstrated (13) that the relative precision,  $\mu_1/M_2$ , does not depend on the absolute amount of carbon dioxide present, if proper judgment is used in the selection of buret and concentration of the standard solution; the relative average deviation of a single adjustment of the phenolphthalein end point has been calculated from the titrations discussed above, and the values  $\pm 1.2\%$  (10 titrations) and  $\pm 1.6\%$  (5 titrations) were found. A value of  $\pm 1.5\%$  appears a fair assumption, if the standard procedure outlined in this paper is carefully followed:

$$1000 \frac{\mu_1}{M_2} = \pm 1.5\%$$

or

$$\mu_1 = 1.5 \frac{M_2}{1000} \quad (6)$$

The precision of the determination of the total carbon dioxide follows from Equation 4:

$$\pi'_{CO_2} = \mu_2' = 1000 \frac{\sqrt{\mu_1^2 + \mu^2}}{M_2}$$

Substitution of the values obtained for  $\mu$ ,  $\mu_1$ , and  $M_2$  in Equations 2, 5, and 6 leads to

$$\pi'_{CO_2} = \pm \sqrt{1.5^2 + \left(0.5 \frac{44 P_{Na}}{23 P_{CO_2}}\right)^2} \% \quad (7)$$

The first item under the root represents the average deviation,  $\pm 1.5\%$ , introduced by the adjustment of the phenolphthalein end point, while the second item takes care of the average deviation,  $\pm 0.5\%$ , of the determination of the titratable base.

DETERMINATION OF SODIUM CARBONATE IN PRESENCE OF HYDROXIDE. The carbonate content is calculated as a direct function of  $M_2$ :

$$P_{Na_2CO_3} = \frac{10.6 NM_2}{S}$$

The relative average deviation,  $\pi'_{Na_2CO_3}$ , which is equal to  $\pi'_{CO_2}$ , is given by Equation 7.



DETERMINATION OF SODIUM HYDROXIDE IN PRESENCE OF CARBONATE. The hydroxide content is calculated as a function of the difference,  $M_1 - M_2 = 2M_1 - M$ . The error,  $\mu_1$ , of the adjustment of the phenolphthalein end point will be doubled in the calculation of the determination. The average deviation is given by

$$\pi'_{\text{NaOH}} = 1000 \frac{\sqrt{(2\mu_1)^2 + \mu^2}}{M_1 - M_2}$$

$$\pi'_{\text{NaOH}} = \pm \sqrt{\left(2 \times 1.5 \frac{40 P_{\text{CO}_2}}{44 P_{\text{NaOH}}}\right)^2 + \left(0.5 \frac{40 P_{\text{Na}}}{23 P_{\text{NaOH}}}\right)^2} \text{ } ^{0/00} \quad (8)$$

DETERMINATION OF SODIUM CARBONATE IN PRESENCE OF BICARBONATE. The carbonate content is a direct function of  $M_1$ , and the relative precision,  $\pi'_{\text{Na}_2\text{CO}_3}$ , is determined by

TABLE II. RELATIVE PRECISIONS OF DETERMINATIONS OF SODIUM HYDROXIDE, SODIUM CARBONATE, AND SODIUM BICARBONATE

(In samples containing sodium carbonate and sodium hydroxide or sodium carbonate and sodium bicarbonate)

NaOH- Na <sub>2</sub> CO <sub>3</sub> Ratio Grams	Na <sub>2</sub> CO <sub>3</sub> - NaHCO <sub>3</sub> Ratio Grams	±π' 0/00 of the Determination of:		
		NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>
10,000:1	.....	0.50	13,800	.....
1000:1	.....	0.50	1300	.....
100:1	.....	0.50	130	.....
10:1	.....	0.56	13	.....
1:1	.....	1.4	2.8	.....
1:10	.....	11	1.8	.....
1:100	.....	120	1.8	.....
1:1000	.....	1200	1.8	.....
1:10,000	.....	12,000	1.8	.....
.....	10,000:1	.....	1.5	25,000
.....	1000:1	.....	1.5	2500
.....	100:1	.....	1.5	250
.....	10:1	.....	1.7	25
.....	1:1	.....	3.4 <sup>a</sup>	5.6 <sup>b</sup>
.....	1:10	.....	19	3.3
.....	1:100	.....	190	3.0
.....	1:1000	.....	1900	3.0
.....	1:10,000	.....	19,000	3.0

<sup>a</sup> Observed, 2.8 and 4.0 parts per thousand.

<sup>b</sup> Observed, 4.3 and 5.5 parts per thousand.

the precision of the adjustment of the phenolphthalein end point only. The average deviation of a single determination is expressed by

$$\pi'_{\text{Na}_2\text{CO}_3} = \mu_1' = 1000 \frac{\mu_1}{M_1} = \pm 1.5 \frac{106 P_{\text{CO}_2}}{44 P_{\text{Na}_2\text{CO}_3}} \text{ } ^{0/00} \quad (9)$$

DETERMINATION OF SODIUM BICARBONATE IN PRESENCE OF CARBONATE. The bicarbonate content is a direct function of the difference,  $M_2 - M_1 = M - 2M_1$ . The uncertainty,  $\mu_1$ , of the adjustment of the phenolphthalein end point is doubled in the calculation of the result of the determination. The average deviation of a single determination is given by

$$\pi'_{\text{NaHCO}_3} = 1000 \frac{\sqrt{(2\mu_1)^2 + \mu^2}}{M_2 - M_1}$$

and

$$\pi'_{\text{NaHCO}_3} = \pm \sqrt{\left(2 \times 1.5 \frac{84 P_{\text{CO}_2}}{44 P_{\text{NaHCO}_3}}\right)^2 + \left(0.5 \frac{84 P_{\text{Na}}}{23 P_{\text{NaHCO}_3}}\right)^2} \text{ } ^{0/00} \quad (10)$$

The relative precisions of Table II have been calculated with the use of the above equations and Equations 11 and 12 which require no comment:

$$P_{\text{CO}_2} = \frac{44}{106} P_{\text{Na}_2\text{CO}_3} + \frac{44}{84} P_{\text{NaHCO}_3} \quad (11)$$

$$P_{\text{Na}} = \frac{23}{40} P_{\text{NaOH}} + \frac{46}{106} P_{\text{Na}_2\text{CO}_3} + \frac{23}{84} P_{\text{NaHCO}_3} \quad (12)$$

The precisions of Table II represent average deviations for single observations, and there is a chance of approximately 3 in 1000 that deviations occur which are four times as large as those listed. The table shows that Ward method becomes unreliable whenever the mass of the determined component is a small fraction of the mass of the second component. An improvement of the precision by refinement of the working technique is possible only for that type of mixtures of little carbonate with much hydroxide, which is indicated in the table by framing with a broken line. The required changes of procedure have been described by Rast (25) and by Han and Chao (8, 9).

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# Dumas Method for Organic Nitrogen

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**D**IFFICULTY is frequently experienced in obtaining accurate results in the determination of nitrogen by the Dumas method, errors sometimes being introduced by too rapid combustion of the sample and by impurities in the carbon dioxide. The error due to too rapid combustion is especially encountered in the analysis of liquid compounds of nitrogen of a semi-explosive nature which tend to dissociate suddenly on heating, and which cannot be analyzed accurately by the Kjeldahl method because of losses during digestion. After considerable experimenting, several modifications of the standard Dumas assembly have been made, with the result that the apparatus described below can be depended upon to give consistently good results even with relatively unstable liquid compounds. Compounds giving "nitrogenous char" and requiring additional oxygen as described by Spies and Harris (1) are not included in the scope of the present apparatus, since these compounds are at the opposite end of the scale so far as ease of combustion is concerned. The present method is concerned with the analysis of compounds which burn too readily rather than too slowly. The modified apparatus makes use of both gas and electric heating, the former to secure the very low, easily controlled heat essential for the proper burning off of the sample. Near the exit end of the combustion tube, the electric furnace is preferable for heating the copper reduction section of the assembly. The complete setup is shown in Figure 1.

## Recommended Modifications

The combustion boat is filled with a mixture of 50 per cent by weight of powdered copper oxide and 50 per cent by weight of calcium carbonate instead of with pure copper oxide. The use of this mixture allows the sample to burn off more slowly, because of the inhibiting effect of the calcium carbonate, and prevents a sudden spurt of gas from forcing its way through the tube immediately after ignition of the sample. Volatile liquids should be weighed in glass ampoules. The ampoule is then laid in the combustion boat and covered with the calcium carbonate-copper oxide mixture, taking care to have the open end of the stem beneath the surface. High-boiling liquids may be weighed directly onto a layer of the mixture in the boat; then, after re-weighing, the boat should be filled to cover the sample.

Pure copper in wire form is used instead of rolled copper gauze in the end of the combustion tube nearest the azotometer, to ensure tight packing of the tube and to obtain close contact of the gases with the surface of the hot copper. Copper in the form of short lengths of wire is more convenient to use than the spiral form and can be more effectively packed in.

The copper is easily made by reducing the regular 0.94-cm. (0.375-inch) length of copper oxide wire with hydrogen gas in a combustion tube.

An electric furnace is used to heat the copper oxide and the pure copper wire in the azotometer end of the tube to a temperature of 650° C., a dull red heat. Gas burners are used to ignite and burn off the sample, starting cold and gradually heating to a maximum of 550° C. The burner under the copper oxide spiral is lighted first. This prevents the gas from receding towards the rear end of the tube. After the spiral is red hot, the second burner is lighted with a low flame to allow the sample to burn off slowly. In this way the rate of gas flow from the burning sample can be regulated very satisfactorily. Towards the end the third burner is lighted to ensure carrying the last traces of gases from the sample into the furnace section.

Temperatures may be determined in advance of actual introduction of the sample by placing a thermocouple in the combustion tube and noting approximate setting of the rheostats and gas flames. A little experience will quickly familiarize the operator with the control of temperature in different sections of the tube.

A convenient method of checking the complete removal of nitrogen from the combustion tube is to take readings at 3- or 4-minute intervals after the combustion is apparently complete, recording the time and volume on a scratch pad. In this way a waste of time is avoided, as the increase in the volume of gas in the azotometer rapidly ceases and a constant final volume varying within only 0.1 ml. is obtained. Determinations may be made in from 35 to 50 minutes, using samples with a total nitrogen content of 0.03 to 0.05 gram of nitrogen.

A two-way stopcock is attached at each end of the train. These are very helpful for the following reasons:

The combustion tube may be swept out with carbon dioxide while the whole apparatus is completely assembled without having to pass the carbon dioxide through the azotometer and reduce the absorptive power of the alkaline solution. Also the carbon dioxide itself may easily be tested for impurities when desired, simply by diverting the flow through the two-way stopcock into the azotometer.

The carbon dioxide supply can be connected to the opposite end of the train during the insertion of the sample. This allows one to reverse the flow of carbon dioxide and prevents air from entering the apparatus while the sample is being pushed into place.

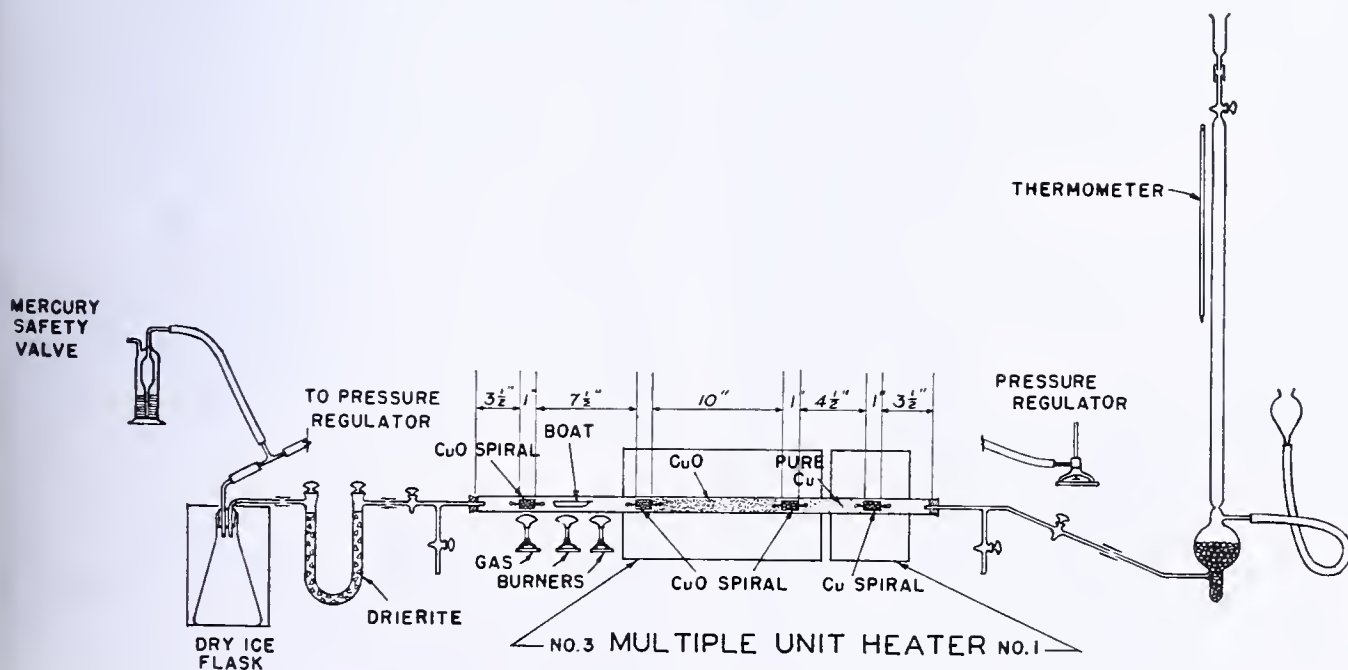


FIGURE 1. DIAGRAM OF SETUP



By careful use of both two-ways, at least 25 determinations may be made without repacking the train, although it may be necessary to burn off the copper spiral plug directly above the first gas burner every 4 or 5 determinations.

The stock azotometer tube has been cut off below the graduations and a bulb sealed on between the graduations and the mercury trap. This bulb is approximately 5 cm. (2 inches) in diameter and is filled with small glass beads. The extra space in the bulb allows the use of an excess of caustic solution and the beads serve to break up the gas bubbles and thus facilitate complete absorption of the carbon dioxide by the alkaline reagent. With this modified azotometer there is no danger of exhausting all the alkali during one determination; in fact, the same solution has been used for two or more determinations.

A satisfactory source of carbon dioxide is dry ice, finely broken up and packed tightly in a 1-liter Pyrex Erlenmeyer flask. Care should be taken in filling the flask to avoid visible air spaces. The mouth of the flask is connected to the rear end of the combustion tube by a piece of bent glass tubing. The flow of carbon dioxide is regulated through a Tirrill burner connected by another piece of glass tubing as shown in Figure 1. A mercury safety valve obviates the risk of breaking the dry ice flask by inadvertent closing of the screw valve of the burner. The rubber stopper through which the outlet tubing passes is wired into the flask to withstand moderate pressure. For safety against possible breakage and to prevent too rapid evolution of carbon dioxide,

the flask is wrapped in a towel or placed in a container or shield of some sort.

This carbon dioxide generator, when set up and adjusted properly, will furnish a dependable supply of pure carbon dioxide for a period of about 10 hours.

The following typical results have been obtained using the assembly:

	Nitrogen Found %	Nitrogen Theoretical %
2-Nitro-3-hexanol	{ 9.42 9.45	9.52
2-Methyl-2-nitro-1-butanol	{ 10.51 10.53	10.53
3-Nitro-4-heptanol	{ 8.65 8.72	8.70
3-Methyl-3-nitro-2-pentanol	{ 9.39 9.42	9.52

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# Methods of Representing Distribution of Particle Size

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**D**ISTRIBUTION of size in a particulate material is commonly represented by plotting either a frequency distribution curve showing the relative number of particles within each range of diameter, or a cumulative curve giving the fraction of the total number of particles which have a diameter greater, or less, than that indicated. The curve from the first method, which is essentially a differential method, resembles a probability curve (see Figure 1), but is usually skewed rather than symmetrical as is the normal probability curve. The second, essentially an integral method, gives an S-shaped curve resembling the ogive or integrated probability curve (Figure 2).

Each method has a number of disadvantages: A relatively large number of experimental points are required to fix the position of the curve, interpolation is sometimes difficult, and extrapolation may be uncertain. Moreover, it is not easy to convert the data from one form to the other unless a great many measurements have been made. When the experimental data give the frequency distribution directly, a large number of observations must be made in order to determine the course of the curve, but when such measurements are available, it is a simple matter to convert them to the cumulative form. When, on the other hand, only data on the cumulative percentage oversize or undersize are available it is by no means easy to obtain the frequency curve, because the conversion involves measuring the slope of the cumulative curve along its length and this is usually uncertain unless the curve is determined by a great many observations. Because of these difficulties numerous efforts have been made to find an equation which fits the distribution curves so that it can be used as a guide in interpolation, extrapolation, and in expressing the form of one curve in terms of the form of the other. The results of these efforts which have been re-

viewed by Work (14), leave much to be desired. The simple relations are not satisfactory, whereas the more successful ones, such as that derived by Rosin and Rammler (12) for broken coal, are somewhat cumbersome to use. It is clear that no single expression will fit the distribution in for all types of material.

An alternative approach to the problem is to use a graphical rather than an analytical method and to devise a mean plotting which reduces the distribution curves to a straight line. If this can be done, the course of the curve can be completely determined, in principle at least, from two experimental observations.

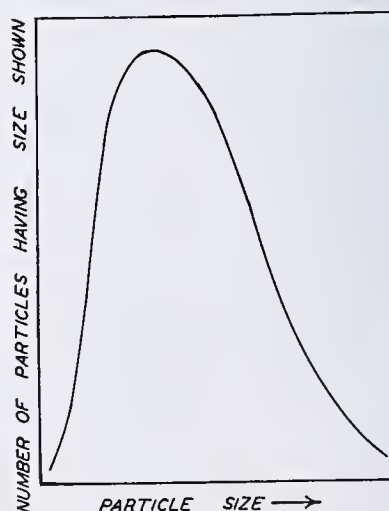


FIGURE 1. SCHEMATIC FREQUENCY CURVE, SHOWING TYPICAL DISTRIBUTION OF PARTICLE SIZE

mental observations and in practice a small number of points commonly suffices if the range covered is relatively wide. In addition, interpolation is easy, the data can be extrapolated with reasonable certainty, and the consistency of a given set of measurements can be judged from the deviation of individual points from the best straight line through the set. Again, no single method has been found which works for all materials, but several methods of plotting



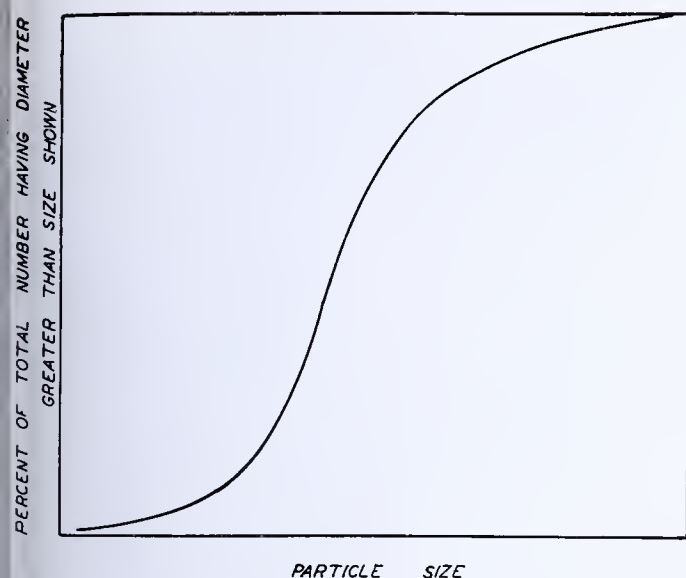


FIGURE 2. SCHEMATIC CUMULATIVE CURVE, SHOWING TYPICAL DISTRIBUTION OF PARTICLE SIZE

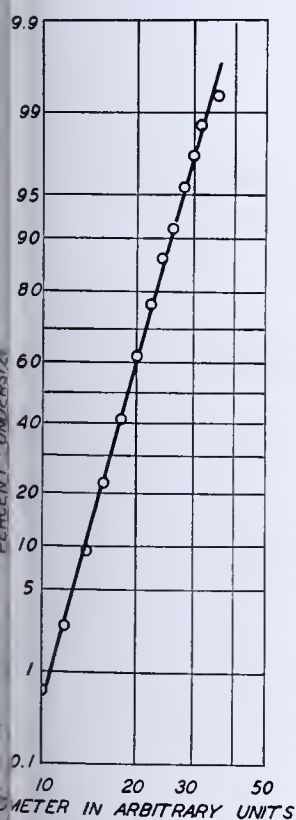


FIGURE 3. LOG-PROBABILITY PLOT OF SIZE DISTRIBUTION IN A SAMPLE OF CRUSHED QUARTZ

technologists, but in each case a knowledge of the method and of its usefulness does not seem to have become widespread. As these methods have wide applicability in industrial chemistry and chemical engineering, it seems desirable to call attention to them, and to compare their usefulness.

### Logarithmic-Probability Coordinates

The most successful of these methods is to plot particle size on a logarithmic scale and cumulative per cent oversize, on a probability scale—that is, a scale whose intervals are based upon values of the probability integral. Graph paper with these coordinates is available, this

method is very convenient. It was first used by Drinker (3) for the size distribution of dusts, was discussed further by Loveland and Trivelli (9), and has been studied in some detail by Hatch and Choate (7) and by Hatch (6). Careful tests by Hatch and Choate show that it holds with satisfactory accuracy for pulverized silica, granite, calcite, and limestone. The author has also used it successfully for a number of other materials, as is illustrated by the lines in Figures 3, 4, 5, and 6, which show typical cumulative curves plotted on log-probability coordinates.

Perhaps the most severe test is that made in Figure 3 with data on ground quartz reported by Martin, Bowes, Coleman, and Littlewood (10). These measurements include observations at relatively short intervals over the whole range of sizes and the final values are the average of nine gradings of a single powder.

Another test on clay, using data reported by Norton and Speil (11), is shown in Figure 4. Again the points fall on a straight line, except for sizes below 0.5 micron. This deviation, which is systematic, may represent a slight systematic error of measurement which is magnified by the extension

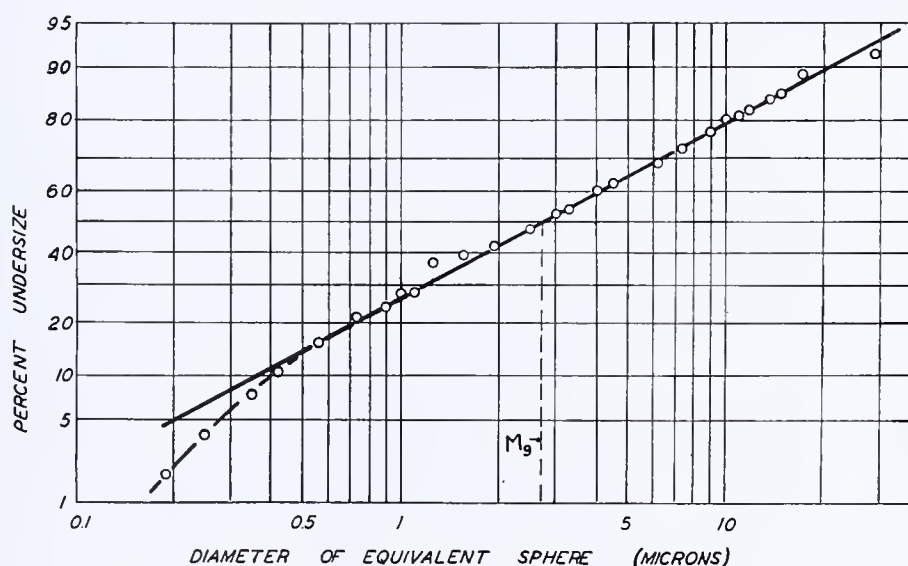


FIGURE 4. LOG-PROBABILITY PLOT OF SIZE DISTRIBUTION IN A SAMPLE OF CLAY

based on the use of special coordinates, have been devised and have been partially successful in that they reduce the cumulative curve to a straight line for a limited group of substances. One of these methods was developed by investigators in the field of public health, another was devised by

of the scale, or it may represent a true departure from the straight-line relationship. Even if it is a real departure, no serious error is introduced by assuming the straight line to hold down to the smallest sizes. For example, at a particle diameter of 0.2 micron the observed value is 2.5 per cent, whereas linear extrapolation from the larger sizes gives 5 per cent. Although this difference appears to be large on the graph because of the extension of the probability scale, it is in fact quite small and in many applications would be negligible.

Figure 5 gives data for soda ash and for sodium bicarbonate reported by Weber and Moran (13). The scatter of the points is greater than in the preceding tests, but there can be little doubt that the data are best represented by a straight line. Curve D in Figure 5 illustrates one advantage of this method of interpretation of the data. Measurements were not made over the whole range of sizes but were confined to particles of diameter greater than 40 microns. When these data are plotted in the ordinary way it is difficult to extend them very far beyond the limit of actual observations, but when plotted as in Figure 5, they can be extrapolated to smaller sizes with some degree of certainty.

Data for powdered alumina reported by Jones (8) are shown in Figure 6. In this case the observations were not tabulated, so that it was necessary to read values from curves;



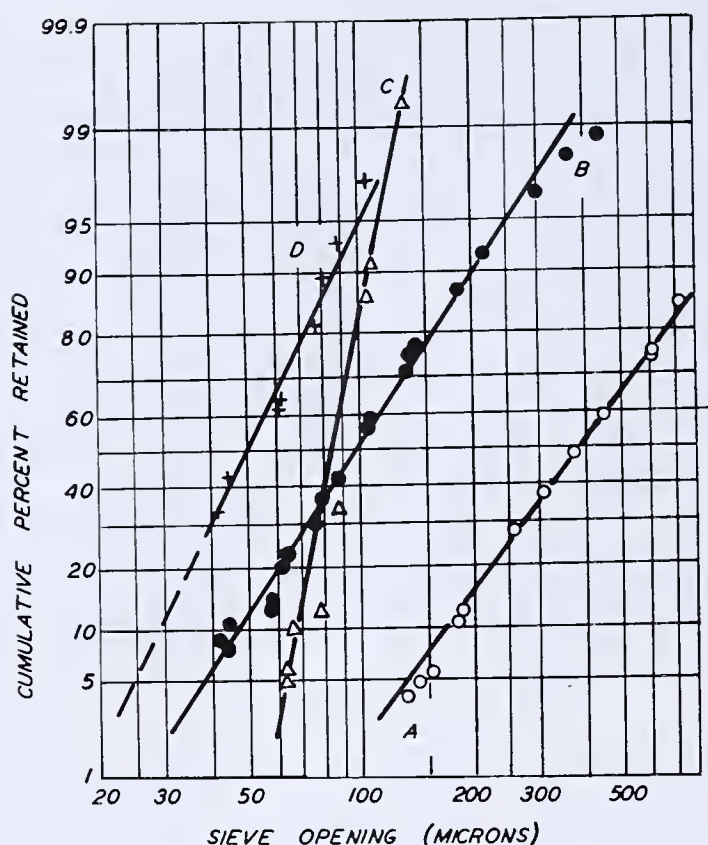


FIGURE 5. LOG-PROBABILITY PLOT OF SIZE DISTRIBUTION IN ALKALI CARBONATES

- A. Dense soda ash
- B. Light soda ash
- C. Granular sodium bicarbonate
- D. Powdered sodium bicarbonate

hence, this test is not to be given the same weight as the others. Nevertheless, it is clear from Figure 6 that the data fall on a satisfactory straight line.

A study of these illustrations reveals the power of the method. If a few observations of cumulative per cent oversize, or undersize, give points which fall on a straight line when plotted on these coordinates, one is reasonably justified in taking this line for the cumulative distribution curve. The frequency distribution curve can then be constructed by taking the change in cumulative percentage for each small

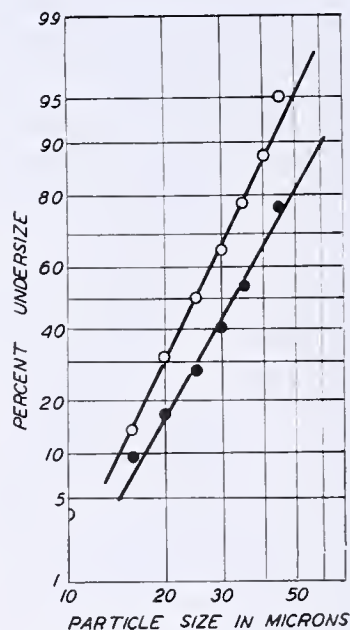


FIGURE 6. LOG-PROBABILITY PLOT OF SIZE DISTRIBUTION IN TWO SAMPLES OF POWDERED ALUMINA

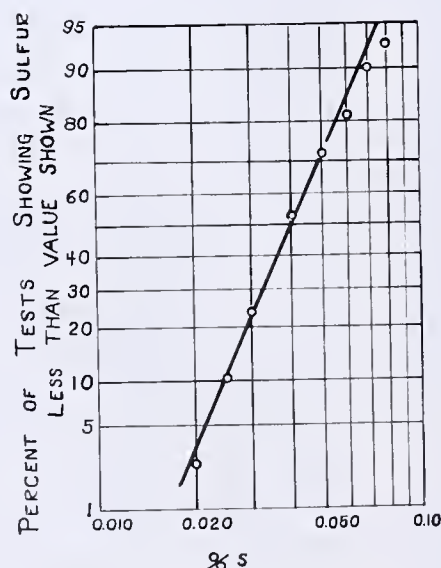


FIGURE 7. LOG-PROBABILITY PLOT OF VARIATION OF SULFUR IN IRON FROM AN "ACTIVE MIXER"

increment of size. This is not the slope of the straight line—that is, the angle with the abscissa—because this is constant but is the change calculated with reference to scales used. In Figure 4, for example, 24 per cent of the particles have diameter less than 0.9 micron and 30 per cent have a diameter less than 1.1 microns, or 6 per cent have a diameter lying between 0.9 and 1.1, which gives a point on the frequency curve.

The examples given in the graphs are all based on distribution by count. It can also be shown (6) that if the distribution gives a straight line, the distribution by weight (screen analysis) is a parallel straight line when plotted on the same coordinates. The exact relation between these lines is discussed in detail below.

In addition to the simple representation of particle size the method has other possible applications. For example, in making concrete aggregates it is frequently desired to have a definite grading of the sand or gravel. If it is once established that the size distribution in the sand or gravel used is represented by a straight line on log-probability paper, an

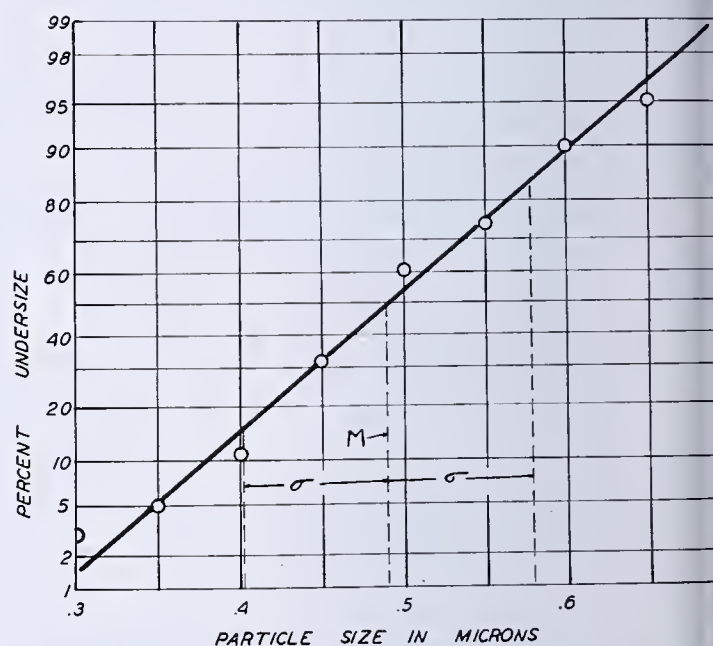


FIGURE 8. ARITHMETIC-PROBABILITY PLOT OF SIZE DISTRIBUTION IN A SAMPLE OF ZINC OXIDE

if the optimum grading is known, then the straight line corresponding to this optimum distribution can be used as a standard and the degree of approach to the desired grading can be determined from a small number of sieve measurements. Again, the straight-line plot may be useful in determining whether or not one has a representative sample of a material for chemical analysis. In some materials, such as certain iron ores, the composition is not uniform but varies with the size of the lumps, so that if a sample contains a larger or smaller proportion of fines than the ore as a whole, an erroneous analysis is obtained. If the grading of the ore as a whole is once established and if this grading plots on a straight line, this line can be used as a standard for other samples. Thus, if two or three screening measurements on a particular sample give points which do not lie upon this straight line, the sample is not representative and should be discarded. It is impossible that a proper selection of fine or coarse particles will give a correct analysis even though the size distribution of the sample does not



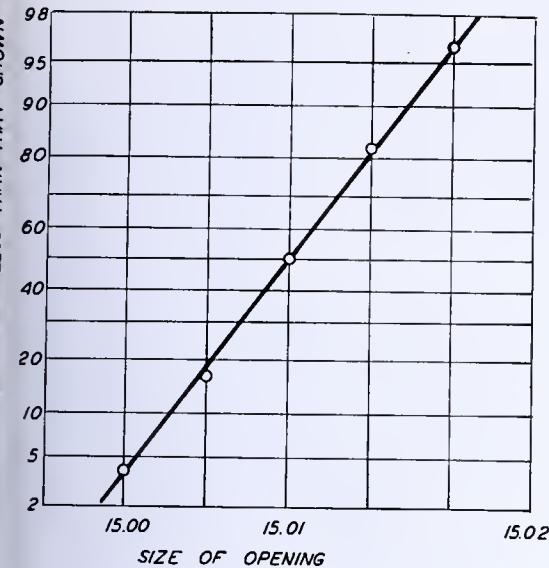


FIGURE 9. ARITHMETIC-PROBABILITY PLOT OF DISTRIBUTION OF DIAMETER AMONG DRILLED HOLES

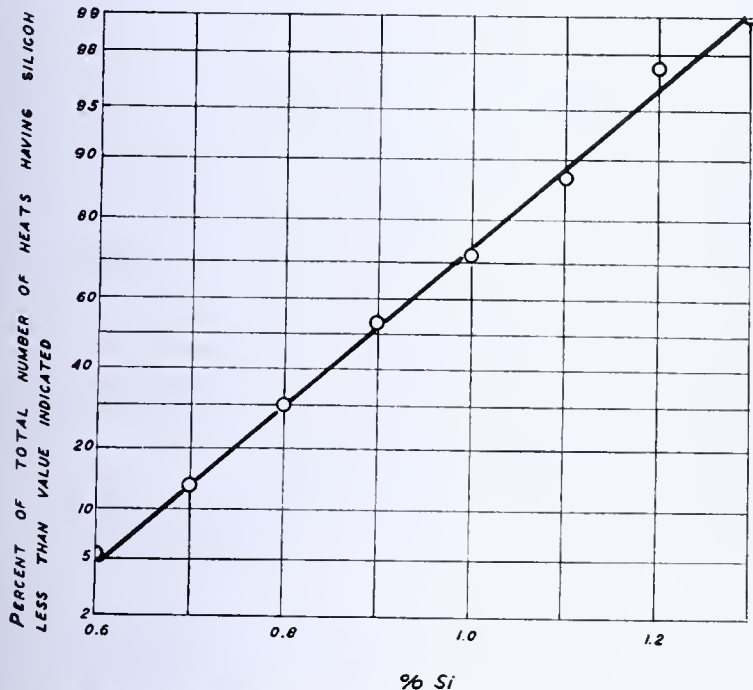


FIGURE 10. ARITHMETIC-PROBABILITY PLOT OF VARIATION OF SILICON IN PIG IRON

substitution of a linear scale of particle size for the logarithmic scale. Graph paper having arithmetic-probability coordinates is easily obtainable and is very convenient for this purpose. Materials which show an approximately normal distribution are relatively rare and are found chiefly among substances produced by a chemical process in which the particles tend to a uniform size rather than among those produced by crushing or grinding. One example is shown in Figure 8 in which data on zinc oxide reported by Green (4) are plotted on arithmetic-probability coordinates.

This method can, of course, be applied to any measurement of size, or indeed, to any variation which follows the normal probability law. This is illustrated by two examples given in Figures 9 and 10. Figure 9, which is based upon data given by Daeves (2), shows the observed variation in size of a number of drilled holes whose nominal diameter was 15.00 mm. In this case, a relatively few observations on the number of holes with diameter above a certain size, which can readily be made by means of several rods of known diameter, enable one to draw the complete distribution curve. Figure 10 shows the variation in silicon content in pig iron produced by a blast furnace over a period of 6 months, and illustrates a close approach to a normal distribution.

### Rosin-Rammler Relation

A third method, which reduces the Rosin-Rammler relation for broken coal to a straight line has been described by Bennett (1). It consists in plotting cumulative per cent oversize on a log-log scale and size of lump on a log scale and is illustrated by the typical example shown in Figure 11. This distribution represents a greater departure from the normal probability distribution than one which gives a straight line on log-probability coordinates. This method of plotting has had notable success for broken coal and Bennett has suggested that it may be applicable to other materials which are brittle and which contain minute cracks at which cleavage may start, but it almost certainly does not have the wide applicability of the logarithmic-probability graph.

In principle, all three of these methods cover the entire range of sizes from zero to infinite diameter—that is, the cumulative per-

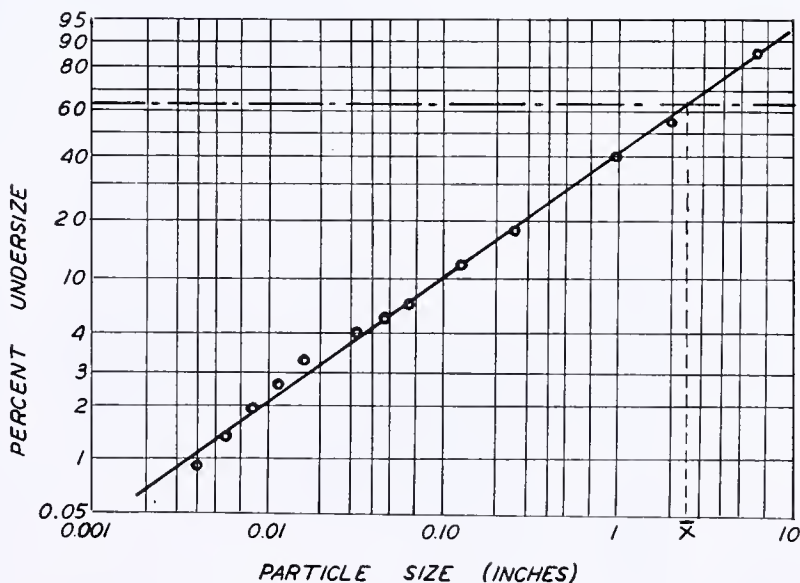


FIGURE 11. SIZE DISTRIBUTION IN RAW COAL PLOTTED ACCORDING TO ROSIN-RAMMLER RELATION (AFTER BENNETT)

perform to the standard, but the chance of obtaining just this selection is very small and it is much safer to use only samples which give a fairly close approach to the grading of the material as a whole. Logarithmic-probability paper can be applied to distributions other than size. For example, Figure 7 shows the distribution of sulfur in iron taken at different times from an "active mixer." The curve obtained with far less labor than that necessary in plotting a frequency or cumulative curve in the ordinary manner.

### Arithmetic-Probability Coordinates

For a few substances, distribution of size approaches the normal probability distribution fairly closely. When this happens the cumulative curve plots as a straight line when particle size is plotted on a linear scale and cumulative per cent oversize, or undersize, is represented on the probability scale. This method differs from the preceding one in the



centage reaches 100 only when the particle diameter becomes zero or infinite—whereas in all measurements the observations cover but a finite range of size, since the cumulative percentage oversize becomes 100 for the smallest particle in the sample, whose diameter is greater than zero, and becomes zero for the largest particle, whose diameter is some finite size. This means that the methods cannot hold rigorously for the extremes in particle size. Experience shows, however, that in practically every case measurable departure occurs only above 99 per cent or below 1 per cent, where observations are least reliable and where the extension of the probability scale becomes enormous. This limitation is, therefore, of little practical significance. It is possible that the deviation at small sizes which appears in Figure 4 may arise from this cause.

### Calculation of Average Diameters

It has been shown by Green (5) that a number of properties of a powder—as, for example, the specific surface (surface area per unit weight)—can be calculated in terms of certain average diameters. The calculation of these diameters is greatly facilitated by the use of these methods of plotting.

The diameter,  $\Delta$ , of a hypothetical particle having average surface area is

$$\Delta = \sqrt{\frac{\Sigma(nx^2)}{\Sigma n}} \quad (1)$$

where  $n$  is the number of particles having diameter  $x$ . Similarly, the diameter,  $D$ , of a hypothetical particle having the average volume is

$$D = \sqrt[3]{\frac{\Sigma(nd^3)}{\Sigma n}} \quad (2)$$

where  $n$  is the number of particles having volume  $d$ . The average surface,  $\bar{s}$ , and the average volume,  $\bar{v}$ , of the particles are then given by

$$\bar{s} = \alpha \Delta^2 \quad (3)$$

$$\bar{v} = \nu D^3 \quad (4)$$

where  $\alpha$  and  $\nu$  are shape factors depending upon the geometric shape of the particles. The specific surface,  $S$ , can be written

$$S = \alpha \Delta^2 / \nu \rho D^3 \quad (5)$$

where  $\rho$  is the density of the particles, assumed to be the same for all. Now the summations  $\Sigma(nd^2)/\Sigma n$  and  $\Sigma(nd^3)/\Sigma n$  can be expressed in terms of quantities which can be taken directly from a graph of the type shown in Figures 8 or 4.

ARITHMETIC-PROBABILITY COORDINATES. The equation for the normal probability distribution is

$$n = \frac{\Sigma n}{\sigma \sqrt{2\pi}} e^{-(x - M)^2 / 2\sigma^2} \quad (6)$$

where  $n$  is the frequency of occurrence of particles having diameter  $x$ ,  $\Sigma n$  is the total number of observations,  $M$  is the arithmetic mean of the diameters, and can be regarded as a constant which fixes the position of the curve, and  $\sigma$  is the standard deviation, which determines the shape of the curve and is numerically equal to the difference between the values of  $x$  for 50 per cent and 84.13 or 15.87 per cent.

Combining Equations 1 and 6

$$\Delta^2 = \frac{\Sigma(nx^2)}{\Sigma n} = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{+\infty} x^2 e^{-(x - M)^2 / 2\sigma^2} dx \quad (7)$$

whence

$$\Delta^2 = M^2 + \sigma^2 + 4\sigma M / \sqrt{2\pi} \quad (8)$$

Similarly, combining Equations 4 and 8

$$D^3 = \frac{\Sigma(nx^3)}{\Sigma n} = \frac{1}{\sigma \sqrt{2\pi}} \int_{-\infty}^{+\infty} x^3 e^{-(x - M)^2 / 2\sigma^2} dx \quad (9)$$

whence

$$D^3 = M^3 + \frac{6M^2\sigma}{\sqrt{2\pi}} + 3\sigma^2 M + \frac{8\sigma^3}{\sqrt{2\pi}} \quad (10)$$

Now  $M$ , the mean size, and  $\sigma$ , the standard deviation, can be read directly from a graph such as is shown in Figure 8,  $M$  being the value of  $x$  for 50 per cent on the ordinate (0.1 micron in Figure 8) and  $\sigma$  being the difference between two values of  $x$  corresponding to 84.13 or 15.87 per cent (0.1 micron in Figure 8). Consequently,  $\Delta^2$ ,  $D^3$ , and in turn  $S$  can be quickly computed.

LOGARITHMIC-PROBABILITY COORDINATES. The equation for the frequency curve using a logarithmic scale for size becomes

$$n = \frac{\Sigma n}{\log \sigma_g \sqrt{2\pi}} e^{-(\log x - \log M_g)^2 / 2 \log^2 \sigma_g} \quad (11)$$

where  $M_g$  is the geometric mean of the values of  $x$ , and  $\sigma_g$  is the geometric standard deviation. The value of  $M_g$  is the value of  $x$  corresponding to 50 per cent oversize and  $\sigma_g$  is given by the ratios

$$\sigma_g = \frac{\text{size at 84.13 per cent}}{\text{size at 50 per cent}} = \frac{\text{size at 50 per cent}}{\text{size at 15.87 per cent}}$$

Both parameters can therefore be obtained from the log-probability graph (see Figure 4).

Equations relating to Green's average diameters to  $M_g$  and  $\sigma_g$  have been derived by Hatch and Choate (7) and are

$$\log \Delta^2 = \log M_g^2 + 4.6052 \log^2 \sigma_g \quad (12)$$

$$\log D^3 = \log M_g^3 + 10.3617 \log^2 \sigma_g \quad (13)$$

$$\log S = \log \alpha / \rho \nu - \log M_g - 5.7565 \log^2 \sigma_g \quad (14)$$

where the symbols have the same meaning as in Equations 5 and 7.

The foregoing relations are based on frequency measurements by count. They have been extended by Hatch (6) to cover size-frequency distributions based on screen analysis and measurement by weight. He has shown that if a given distribution follows the logarithmic-probability relation by count it must also follow it when measurements are made by weight (screen analysis); moreover, the curves for the two distributions plot as parallel lines on log-probability paper. The conversion can be made on the basis that

$$\log M_g = \log M_g' - 6.9078 \log^2 \sigma_g' \quad (15)$$

where  $M_g'$  and  $\sigma_g'$  are, respectively, the geometric mean and geometric standard deviation derived from the weight (screen analysis) curve. Screen measurements for this purpose should be carried out with sieves which have been calibrated by methods which are described in detail by Hatch.

ROSIN-RAMMLER EQUATION. The Rosin-Rammler equation as given by Bennett (1) is

$$R = 100 e^{-(x/\bar{x})^b} \quad (16)$$

where  $R$  is the percentage of the total number of particles which have a diameter greater than  $x$ , and  $\bar{x}$  and  $b$  are constants which characterize the distribution for each sample. (The symbol  $b$  has been substituted for the  $n$  used by Bennett in order to avoid confusion with the symbol used for normal



number of particles having a given diameter.) The parameters  $\bar{x}$  and  $b$  can be evaluated from a graph such as is shown in Figure 11. Equation 18 shows that when  $x = \bar{x}$ ,  $y = 100/e = 36.79$  per cent, so that the value of  $x$  can be read directly as that value of  $x$  at which the percentage over-size is 36.79, or at which the percentage under-size is 63.21. This is illustrated in Figure 11 by the intersection of the line of the size distribution with the dot-dash horizontal line at  $R = 63.21$  per cent, in this case,  $\bar{x} = 6.25$  cm. (2.5 inches). The constant  $\bar{x}$  is therefore a measure of the magnitude of the size of the particles considered and in this respect is analogous to  $M$  and  $M_p$  in the preceding equations. The value of parameter  $b$  is given by the slope of the curve. It is a measure of the dispersion of the distribution, that is, if  $b$  is large, the particles are closely grouped in diameter, whereas if  $b$  is small, the particles are distributed over a relatively wide range. The constant  $b$  is therefore analogous to  $\sigma$  in the preceding equations.

The form of Equation 17 makes it difficult to express Green's average diameters, or the specific surface, in terms of  $\bar{x}$  and  $b$ .

### Summary

It is desirable for many reasons to be able to plot a cumulative size-distribution curve as a straight line. If this can be done, the number of measurements can be reduced, interpolation becomes easier, extrapolation becomes more reliable, the consistency of the observations can be judged at a glance, the calculation of average diameters is facilitated, and the frequency distribution curve can be readily obtained. No single method of plotting which is applicable to all materials has been found, nor is it likely that one exists. There are, however, three methods which have proved successful for

certain classes of substances. The most widely applicable one is to plot particle size on a logarithmic scale and cumulative per cent on an integrated probability scale. It gives satisfactory results for crushed or ground materials such as silica, granite, limestone, clay, sodium carbonate, and alumina. The second is the Rosin-Rammler method which plots size on a log scale and cumulative per cent on a log-log scale; it has been notably successful with broken coal. The third method, which appears to have only a very limited applicability, is to plot size on a linear scale and cumulative per cent on the integrated probability scale.

These methods have a possible application to the determination of whether or not one has a representative sample on a material whose composition varies with size of lump, and can even be extended to distributions other than size, such as the variation with time of the composition of pig iron from a given furnace.

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## Improved Form of Jones Reductor

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IN THE course of analytical work which involved the estimation of iron, the authors have found a modified form of Jones reductor very convenient.

In the usual form (1), shown at right of Figure 1, hydrogen collects just below the zinc column and cannot escape freely. This gives rise to two disadvantages in manipulation: (1) The free and steady flow of the acid solution is impeded. (2) In resetting the reductor for a fresh experiment the zinc has to be washed thoroughly and all the accumulated gas displaced by distilled water, and since this cannot be accomplished easily either by passing a swift stream of water through the reductor or even by applying suction, it often becomes necessary to remove the reductor from its support to displace the gas. The improved form obviates both these difficulties. The wide tube is bent downward at the bottom, as shown, and the gas which collects below the zinc rises in the narrow tube and is automatically displaced out by the solution. Hence, it does not accumulate to any undesirable

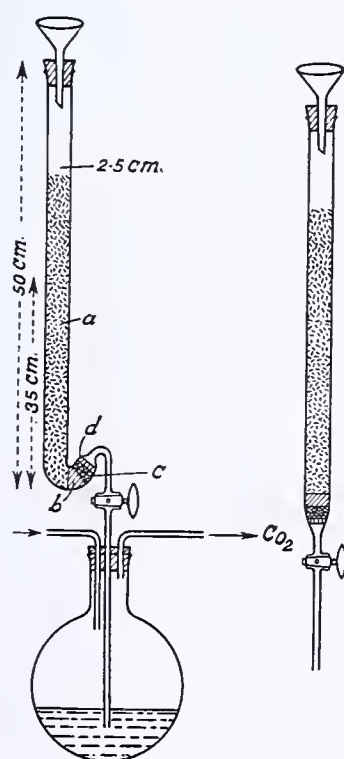


FIGURE 1. JONES REDUCTOR

- a. Amalgamated zinc granules
- b. Glass wool or asbestos pulp
- c. Glass beads
- d. Perforated porcelain disk

extent and thereby impede the flow. For washing the apparatus finally and for displacing any remaining gas bubble before commencing a fresh experiment, all that is necessary is to run down water in a brisk stream through the tube with the stopcock fully open.

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# Large-Size Extractor for Liquids

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DURING the isolation of certain alkaloids from aqueous concentrates, it became necessary to employ some method whereby sizable quantities of solution could be extracted continuously with ether until alkaloid-free. Although many authors (1, 2, 4, 5, 7) have described large-scale apparatus for the extraction of solid material, the writer has been unable to find in the literature any description of a plant-size extractor for liquids. Employing the principles embodied in the liquid extractor described by Palkin (6), an apparatus has been built for the extraction of 40-liter batches of liquid by lighter-than-water solvents.

## Description of Extractor

As shown in Figure 1, *A* is a glazed earthenware 60-liter crock equipped with lid. A hole 25 mm. in diameter has been drilled in the center of the lid, and a similar hole drilled in the side of the crock about 15 mm. above the 40-liter level. *B* is an ice bath

used when the material being extracted is unstable at room temperature. *C* and *C'* represent six hollow cylinders sealed at one end and constructed of Aloxite brand porous corundum (medium grade). These cylinders are attached by corks to the six legs of a radial glass manifold, which, in turn, is connected by means of 15-mm. glass tubing to the 500-cc. aspirator bottle, *E*. The remaining parts of the extractor consist of three Allihn condensers, *F*, *F'*, *F''*, a spherical condenser, *G*, a 12-liter Pyrex balloon flask, *I*, and miscellaneous glass fittings such as are found in every laboratory. *K* is made of 40-mm. glass tubing, the short leg of which has been tapered to meet the T-tube at *L*. *M* is a cork "umbrella" to prevent condensed moisture from running into *E*.

## Operation of Extractor

The aqueous concentrate to be extracted is placed in *A* and, if necessary, is diluted to 40 liters. The solvent (ether in this case) is placed in *I* along with the necessary acid solution, if the alkaloid is to be converted immediately into a salt. The solvent is brought to a boil by means of water bath *J*, the vapor passes up through *K*, is condensed by *F*, *F'*, and *G*, and drops into *E*. The purpose of *E* is to enable the operator to follow the rate of flow. The solvent passes from *E* down into the porous cylinders, from which it emerges as a fine spray. As this spray rises through the aqueous liquid, it extracts the alkaloid and spills through the side outlet back into *I*. *F''* prevents hot vapors from *I* from passing into *A* and heating the liquid. Portions of solvent are drawn off at *N* from time to time and tested chemically to determine completion of extraction.

This extractor has been in use in the writer's laboratory for over a year for the extraction of the recently discovered ergot alkaloid, ergonovine. At an approximate concentration of 0.025 per cent this particular alkaloid is completely extracted by ether in 10 to 12 hours' operation of the extractor, as evidenced by a negative test with Glycart's modification of Smith's reagent (3). Less than 500 cc. of ether is lost during an 8-hour extraction. The size of the setup can be varied to accommodate the volume of liquid to be extracted.

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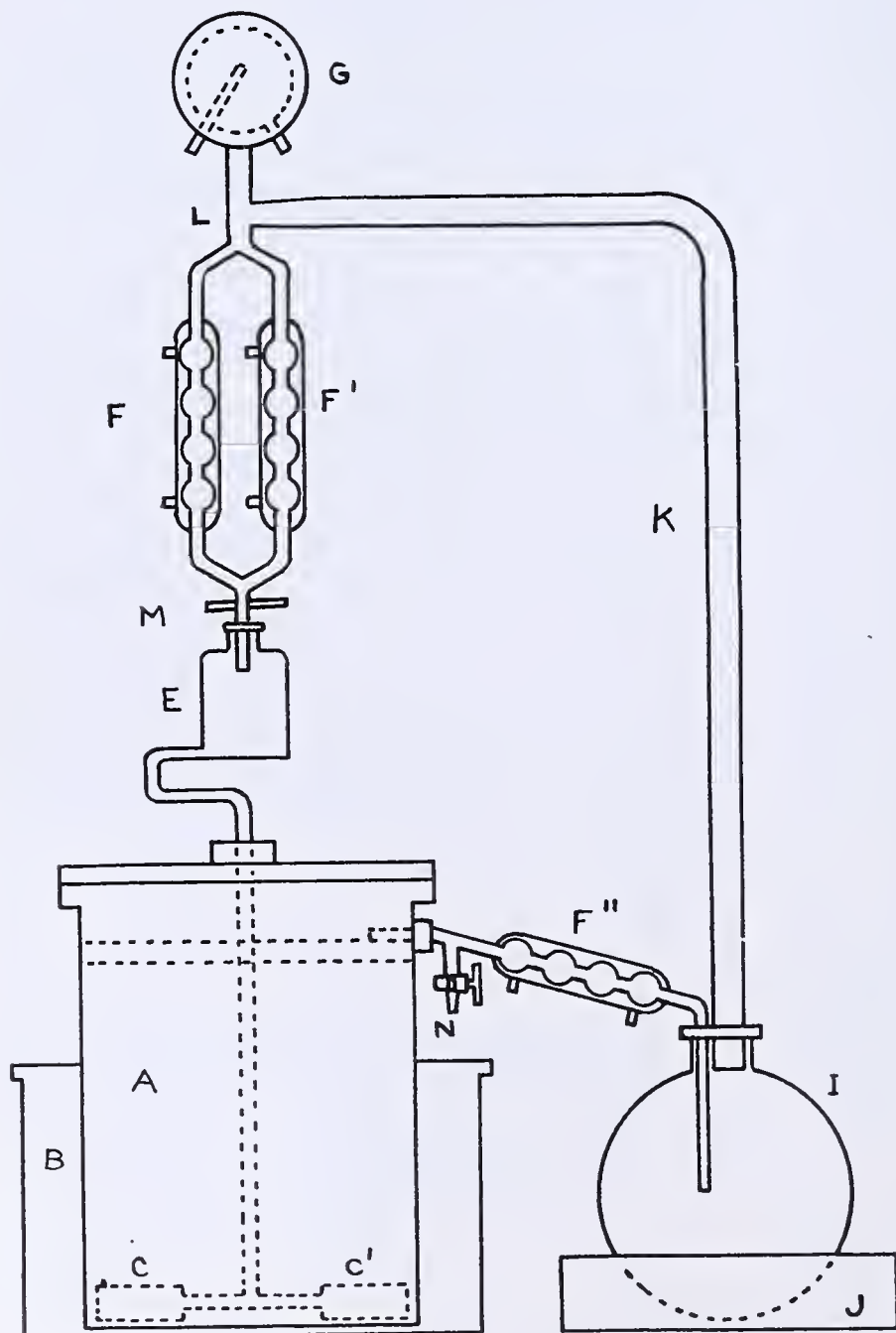
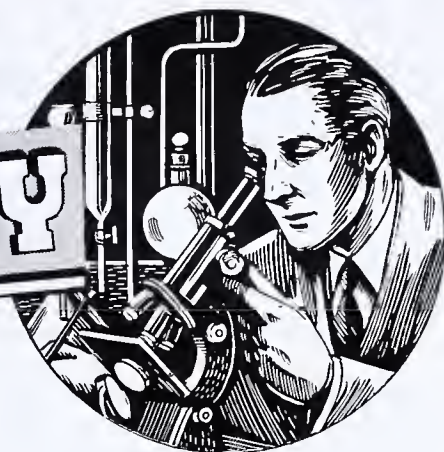


FIGURE 1. DIAGRAM OF EXTRACTOR



# MICROCHEMISTRY



## The Services of Émile M. Chamot to Chemical Microscopy

THE origin and advancement of a field of science are rarely to be ascribed to one man; Émile M. Chamot's modesty would prevent him from accepting credit for creating chemical microscopy, but his pioneer work in developing it and in encouraging its application certainly entitles him to be called its foremost exponent if not its father.

It was not merely a case of the time's being ripe; although valuable methods and facts were already available in chemistry and in allied sciences, and microscopes were beginning to be used in chemistry and technology, the work was scattering and unrelated, its value was not generally recognized, and chemists showed little interest in the microscopical approach to their problems.

Chamot's work involved the organization of existing information and its presentation in a form usable by chemists, together with the development of methods and instruments

suitable for the variety of work encountered in technical laboratories. Besides this, he had to do a great deal of what he calls "preaching", by precept and example, to show chemists how illuminating microscopical studies can be, and how economical of time and labor. All this was inspired, not by any desire to glorify micromethods for their own sake or to monopolize a specialty, but simply because of his tireless personal enthusiasm for the work and because he was convinced of its general value.

Chamot's services as a chemist, a teacher, and a citizen have previously received tribute (2), but his unique role in the development of chemical microscopy can best be appreciated in terms of his career.

### Education

As a boy in Buffalo, his birthplace, he enjoyed the formative hobby of nature study with the Naturalists' Field Club, and was encouraged in biological and mineralogical pursuits that proved invaluable adjuncts to chemistry and microscopy.

In his student days at Cornell, his life interest was probably conditioned by his senior thesis under G. C. Caldwell in 1891, for it involved a great deal of microscopical work on the various crystalline phases obtained in the hydrolysis and reduction of lead nitrate and nitrite. During the summer he supplemented this study by photomicrography of his preparations. [Caldwell's appreciation of the value of chemical microscopy was evidenced by more than one instance—a classmate, Lomax, had as a thesis topic the microscopical identification of alkaloids based on Wormley's methods (5).] This, together with emphasis on plant constituents and toxicology in analytical chemistry under Caldwell, undoubtedly stimulated Chamot's interest in the organic aspects of microscopy.

A year in Europe, after receiving his doctorate in 1897, was important, not primarily because of the training in toxicology with Macé, its primary objective, but because it brought him in contact with Behrens at Delft. Chamot had previously familiarized himself with Behrens' system of inorganic qualitative microscopical analysis (1) but was fortunate in sharing in the detailed instructions which Behrens was giving to Kley, his new assistant, in preparation for the course that was about to be offered formally for the first time. Chamot was thus perhaps Behrens' first pupil. On leaving, he asked how he could repay his master; the reply was "Start some courses in America." Chamot has repeatedly acknowledged his indebtedness to Behrens, whose novel methods and reagents still stand as the greatest contribution to chemical microscopy and have been improved but not supplanted by the work of



ÉMILE M. CHAMOT



his followers, Emich, Donau, Schoorl, Denigès, Haushofer, Klement and Renard, and others.

### Development of Chemical Microscopy

The first fruit of Chamot's studies was a series of papers on microchemical analysis which appeared in the *Journal of Applied Microscopy* between the years 1899 and 1902. In them he described a chemical microscope, which Bausch & Lomb had just produced in accordance with his specifications, and reviewed the equipment and methods for microscopical qualitative analysis; many original illustrations and new procedures were included.

As early as 1900, the Department of Chemistry at Cornell was offering two formal courses in microchemical analysis, a term each of inorganic and organic; in 1902 microscopy of foods was also given. (A photograph of the main chemistry lecture room in 1889 shows large charts of interference figures, and a 1-hour course in microscopy appeared in the announcement for 1890; evidently Caldwell's interest considerably antedated Chamot.) These are probably the earliest courses in America in this field, though Hinrichs (3) at St. Louis was active at about this time. Instruction in chemical microscopy has continued at Cornell since the beginning of the present century, and Chamot continually developed and extended its scope; because he held at different times instructorships in almost all the courses of the department he was peculiarly fitted to recognize the value and the relationships of microscopical methods to the various divisions of chemistry in academic, forensic, and technical work.

Fortunately, Caldwell's successor as head of the department, L. M. Dennis, believed strongly in the value of optical methods (courses in polarimetry and refractometry and in spectroscopy were offered as early as 1892), and Chamot was able to build up the equipment of the laboratory as need arose; a photograph shows at least nine microscopes in 1905, and twenty or more in 1915.

At first the courses offered were primarily in microscopical analysis; soon it became evident, from Chamot's own experience and from that of his students, that many other aspects of microscopy were of potential value to chemists in industry and research, and a course in general microscopical methods covering micrometry, quantitative estimations, and crystal studies was offered. At an alumni conference it was recommended that training in microscopical methods be required of all students specializing in chemistry at Cornell and when the degree of bachelor of chemistry was established in 1911, such a course was made part of its curriculum and has continued, although the degree has been superseded by that of chemical engineer. At a rough estimate, between two and three thousand American chemists have had at least an introductory training directly under Chamot, and although only a fraction of these may have done much subsequent microscopical work, they have all had the benefit of his critical thinking and emphasis on careful observation and interpretation, as well as a vivid recollection of the small-scale aspects of chemical phenomena so unforgettably demonstrated in the laboratory experiments which he devised.

Chamot's influence outside his classes was ever widening, by lectures and consultation, continually stressing the importance of direct and rapid microscopical approach to new problems of industry and research. His stories of actual cases from his own vast experience, where a close-up showed holes in what appeared to be a blank wall, are still remembered by those who had the pleasure of hearing him at meetings of local sections and other societies.

At first he had, like Behrens, used the term "microchemistry", but with his growing realization of the importance of physical and physicochemical factors in chemical behavior,

and with the contemporary development of quantitative microanalysis by Emich and Pregl, he felt the need for a designation of the miscellaneous related kinds of microscopical work that chemists have to do, and coined the term "chemical microscopy" about 1914.

In 1915, his "Elementary Chemical Microscopy" embodied in book form the instruction that had hitherto been available only to his students. The reception of this work and of its successor, "Handbook of Chemical Microscopy", by chemists and workers in allied fields is indicated by the fact that their purchases have always far exceeded those for class use. Chamot's service to American chemistry was rendered more than inspirational, for he supplied the first compendium of selected information and methods of real utility to the independent investigator, not only for the analysis of minute samples but for technical studies where preparation methods and observations of physical conditions or properties were of primary importance. Chamot's book greatly aided in the spread of instruction in chemical microscopy, by his students or by faculty members in other institutions. By 1920, one or more courses closely patterned after those at Cornell were being offered in at least three other universities, and the number has increased several times since then.

As his students have gone out into industry they have carried his inspiration, and have been willing to "try the microscope first instead of last." In many of the larger research and control laboratories extensive applications of chemical microscopy have been the direct result of his teachings and of his forceful presentation of its potentialities in new fields.

His influence has not been confined to America; students from abroad, correspondence with investigators in other countries, and references to his work in foreign journals attest this. In 1924-25 he was an exchange professor in France, representing seven eastern universities. His lectures and conferences at a score or more of educational institutions aroused much interest in chemical microscopy, and were an important contribution to science in the country of his forebears.

Unfortunately, during this busy period of absence, the Technical Photographic and Microscopical Society, of which he was a founder and the first president, declined and has since been disbanded, but its existence was indicative of the dissemination of microscopical methods in various fields of technology at that time. Their importance received official emphasis in the following statement, from the report of a committee of the National Research Council, on "The Education of the Research Chemist": "The microscope has come to be so valuable a part of research laboratory equipment that every research chemist should be well trained in its use" (4). Chamot's "preaching" was the direct cause of this attitude and of the leadership which American chemists have maintained in the broader applications of chemical microscopy.

Modest and shunning publicity, Chamot has given freely of advice and experimental assistance in innumerable investigations, without thought of personal recognition. His knowledge of biology has been invaluable, not only in his early work on toxicology and in his later development of sanitary chemistry and food analysis at Cornell, but also because it enabled him to cooperate with botanists, animal histologists, and bacteriologists, with intelligent insight and novel and convincing microscopical methods of attack.

The services of Professor Chamot received conspicuous recognition by the award in 1937 of the Longstreth Medal of the Franklin Institute "for meritorious work in chemical microscopy", but he derives far greater satisfaction from the contributions his students have made to the extension of this field, and from the increasing utilization of its methods by chemists, geologists, biologists, and metallurgists.



Relieved from teaching duties, he continues active in research and writing. Long may the light of his life work illuminate chemical microscopy; its secondary radiations will ever continue to clarify obscurity of observation and interpretation in the realm of microns.

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# Determination of Bismuth in Biological Material

## A Photometric Dithizone Method

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RECENT experimental studies on the physiological behavior of bismuth required an adequate analytical method for dealing with less than 5 micrograms in biological material.

A spectrographic method has been developed by Cholak (3) by means of which quantities of 1 microgram or more can be determined, but the literature failed to disclose the existence of a chemical method with the requisite sensitivity. Tompsett (8) has described a method for the determination of bismuth in biological material using thiourea following the isolation of bismuth with diethyldithiocarbamate, but he gives no analytical data and does not discuss the application of the method to amounts of bismuth below 5 micrograms. Haddock (6) determines bismuth colorimetrically as the iodobismuthite ion following its isolation with dithizone, but his method applies only to values between 5 and 100 micrograms. Fischer (5) pointed out the high sensitivity of dithizone in the detection of bismuth, and suggested the possibility of using a "mixed color" technique in the determination of bismuth with dithizone (4).

A method based on these suggestions is reported herein. Unlike lead (7), however, bismuth is not extracted quantitatively from mixtures of extraneous salts and must therefore be isolated as the sulfide before proceeding with the dithizone extractions. The method has the necessary sensitivity and has proved reliable for all ranges of concentrations likely to be encountered.

### Reagents

Ordinary high-grade chemicals may be used for all steps up to the point of separation of bismuth from lead (extraction 2). Since any lead present in the reagents used beyond this point is estimated as bismuth, reagents for the final step must be purified. The precautions to be taken are as follows:

Ammonia used to prepare the ammonia-cyanide mixture is freshly distilled in glass. Potassium cyanide as a 50 per cent (weight by volume) aqueous solution is treated with dithizone in chloroform (20 mg. per liter), the dithizone entering the aqueous phase being reduced to a minimum by repeated treatment with clear chloroform (2). The purified solution is then diluted with distilled water to the proper strength as required for the ammonia-cyanide mixture (7). The dithizone used to prepare the extraction solutions for extractions 2 and 3 is purified and the chloroform used for solution is redistilled and specially treated to prevent oxidation, by methods previously described (1, 7). Nitric acid (1 + 99) used in extraction 2 is prepared from nitric acid once distilled in quartz (specific gravity 1.40) and the distilled water is further redistilled from a Pyrex glass still.

### Glassware

The graduated Squibb (Pyrex) separatory funnels used (7) must be cleaned meticulously with hot nitric acid (1 + 1) and

distilled water to ensure removal of any bismuth present as surface contamination from previous use. This cleansing must be repeated for funnels used in extraction 2 to prevent contamination by surface lead.

### Apparatus

A Bausch & Lomb spectrophotometer is employed for density measurements. Readings are taken with the monochromator set of 505 mμ. The instrument is equipped with matched pairs of cells, which have been described previously (7).

### Procedure

**PREPARATION OF SAMPLES.** Samples of biological material are prepared for analysis by dry or wet ashing methods as described by Cholak (3) except that 1 mg. of copper is added to serve as an entraining agent during the isolation of bismuth as the sulfide. The filter paper containing the sulfides is treated with 25 ml. of nitric acid (1 + 9), in the original beaker used for gassing, and the mixture is gently heated to effect solution of the sulfides. The filter paper and free sulfur are removed by filtration through a type 3G4 filter of fritted glass (Jena). After alternate washing of the filter with hot nitric acid (1 + 1) and hot distilled water, the filtrate and washings are returned to the original beaker and evaporated to low volume.

**EXTRACTION 1 (REMOVAL OF COPPER).** The sample thus prepared is transferred to a 125-ml. graduated Squibb-type separatory funnel by alternately washing the beaker with hot nitric acid (1 + 1) and with hot distilled water. After dilution to 50 ml., 3 drops of thymol blue (Clark and Lubs) and 5 ml. of potassium cyanide solution (10 per cent weight by volume) are added and the pH of the solution is adjusted to 9.5 with concentrated ammonia. Bismuth and lead are extracted as the dithizonates by successive additions of 5-ml. portions of dithizone in chloroform (20 mg. per liter). The number of 5-ml. portions used serves as a preliminary guide to the amount of bismuth present, since each 5-ml. portion extracts approximately 25 micrograms of bismuth. Bismuth dithizonate imparts a bright orange color to the chloroform phase. The last 5-ml. portion, which should show no change in color, is withdrawn as completely as possible. The aqueous layer is shaken twice with 2-ml. portions of clear chloroform and the chloroform phases are added to the previous extracts. The aqueous phase is then treated with 2 ml. of concentrated nitric acid and the solution is readjusted to pH 9.5 with dilute ammonia (1 + 9). Ten milliliters of dithizone solution are then added as above and withdrawn, followed by one 5-ml. portion. The combined extracts containing bismuth and lead dithizonates plus uncombined dithizone in chloroform are next washed with 25 ml. of distilled water. After separation of the two phases the aqueous phase is shaken twice with 2-ml. portions of clear chloroform; the latter are added to the chloroform phase, but the wash water is discarded.

Depending upon the amount of bismuth present, either the whole or an aliquot of the total extract containing not more than 50 micrograms of bismuth is taken for extraction 2. This is shaken twice with 25-ml. portions of nitric acid (1 + 99). The chloroform-dithizone phase is discarded and the collected acid phase is treated with clear chloroform to expell the last traces of the dithizone-chloroform phase.



EXTRACTION 2 (REMOVAL OF LEAD). To the acid aqueous phase obtained above, 3 drops of *m*-cresol purple (Clark and Lubs) are added and the pH of the solution is adjusted to 2 by the addition of dilute ammonium hydroxide (1 + 9). Bismuth is now extracted by successive additions of 5-ml. portions of dithizone in chloroform (20 mg. per liter) in the same manner as in extraction 1, except that the dithizone solution used is treated with nitric acid (1 + 99) to ensure removal of lead. The range is now definitely placed and the chloroform fractions are collected in a clean separatory funnel. (Separatory funnels used for this step as well as the step to follow must be scrupulously clean.) Bismuth free from lead (9) is now brought into solution as the pure nitrate in 50 ml. of nitric acid (1 + 99) by the use of two 25-ml. portions of acid as in extraction 1.

EXTRACTION 3 (ESTIMATION OF BISMUTH). For the final estimation, bismuth is extracted a third time by means of chloroform-dithizone solutions of various strengths, depending upon the range. The technique of estimation is identical with that described previously for lead (7) except for the following modifications:

1. The 50 ml. of nitric acid (1 + 99) containing pure bismuth nitrate are freed from entrained chloroform either by applying air suction over the surface to remove droplets of chloroform or by normal evaporation. Excess chloroform at the base of the liquid is drawn off as completely as possible (2).
2. Potassium cyanide, purified as described under "reagents", is used to make the ammonia-cyanide mixture.
3. To guard against lead contamination the chloroform phase containing bismuth dithizonate plus excess dithizone is removed directly through the funnel stem into the proper-sized cell (2), traces of water in the stem having first been removed by swabbing with an ordinary pipe cleaner folded at one end to produce a snug fit.
4. A reagent blank need not be considered since bismuth is not a common contaminant of reagents used (3).
5. The ammonia-cyanide mixture and all chloroform solutions of dithizone are stored in a refrigerator to increase their stability (2). As a further safeguard the dithizone solutions are stored in lightproof containers.
6. The concentrations of the various dithizone solutions have been increased, as shown in Table I.

TABLE I. DITHIZONE CONCENTRATION

Range Micrograms	Dithizone Concentration Mg./liter	Volume Used Ml.	Cell Mm.
0- 5	6	10	50
0-25	12	25	25
0-50	24	25	12

Working curves obtained for the various ranges by the use of pure bismuth nitrate solution in chloroform-saturated nitric acid (1 + 99) are obtained in a manner similar to that used for lead (7). The slopes of the curves for corresponding ranges are somewhat steeper, however, in the case of bismuth. Pure metallic bismuth is used to prepare the nitrate solutions.

Analytical Results

In Table II are listed results obtained by the analysis of 100-ml. urine samples (in triplicate) containing known added quantities of bismuth. In Table III are listed results obtained by the analysis of 10-gram samples of rabbit blood (in triplicate) containing known added quantities of bismuth.

Discussion

Interfering elements are stannous tin, monovalent thallium, and lead. Stannous tin is oxidized and removed during the course of analysis (7). Monovalent thallium and lead are removed during extraction 2; the former, however, has not been encountered in biological material. In order to prevent the precipitation of Ca<sup>++</sup>, Fe<sup>+++</sup>, and PO<sub>4</sub><sup>---</sup> ions when the solutions are adjusted to pH 9.5, excessive amounts of ammonium citrate must be added. When this has been done the writer has been unable to extract bismuth quantitatively from prepared solutions of biological material such as blood and urine, even though he followed the procedure, outlined by Haddock (6), of using a relatively strong chloroform-dithizone solution (1 gram per liter) for extraction. However, no difficulty was encountered when

the bismuth was first isolated as the sulfide, copper being used as the entraining agent to effect the removal of minute quantities. The excess copper added does not complicate the method, since it is "complexed out" by means of potassium cyanide in the first extraction.

TABLE II. ANALYSIS OF URINE

Range Used Micrograms	Bismuth Added Micrograms	Bismuth Found Micrograms
0- 5	Nil	0.1
0- 5	Nil	Nil
0- 5	Nil	0.1
0- 5	1.0	1.1
0- 5	1.0	1.0
0- 5	1.0	1.2
0- 5	5	4.8
0- 5	5	4.9
0- 5	5	5.0
0-25	15	14.5
0-25	15	15.0
0-25	15	15.0
0-50	50	49
0-50	50	50
0-50	50	50
0-50	500	470
0-50	500	470
0-50	500	480

However, excessive amounts of potassium cyanide entrained in the combined extract obtained during extraction 1 subsequently prevent the complete extraction of bismuth as the dithizonate from the acid phase adjusted to pH 2. For this reason the combined dithizone extracts are washed with distilled water before proceeding to the conversion of the bismuth dithizonate to bismuth nitrate with nitric acid (1 + 99). All the potassium cyanide is not removed, but the portion remaining is not harmful.

TABLE III. ANALYSIS OF BLOOD

Range Used Micrograms	Bismuth Added Micrograms	Bismuth Found Micrograms
0- 5	Nil	Nil
0- 5	Nil	0.1
0- 5	Nil	0.2
0- 5	1.0	1.2
0- 5	1.0	1.0
0- 5	1.0	1.0
0- 5	2.5	2.6
0- 5	2.5	2.4
0- 5	2.5	2.5
0- 5	5.0	5.0
0- 5	5.0	4.9
0- 5	5.0	5.0
0-25	15	15
0-25	15	15
0-25	15	14.5
0-50	50	47
0-50	50	48
0-50	50	48

Particularly important was the discovery that when quantities of bismuth in excess of 50 micrograms are extracted during extraction 1, some bismuth dithizonate as well as some pure dithizone remains in the aqueous phase. This is due, of course, to the partition coefficient of the bismuth dithizonate between the two phases. The greater solubility of the bismuth dithizonate in chloroform suggested a means for partially overcoming this difficulty: The aqueous phase following its initial apparent complete extraction is reacidified with nitric acid, and extracted again with dithizone after again adjusting the pH to 9.5. Preliminary washing of the extracted aqueous phase with the 2-ml. portions of clear chloroform is also beneficial, since an appreciable amount of bismuth dithizonate is removed from the aqueous phase—frequently it is enough to cause a decided color change in the chloroform used. The following experiment indicates the magnitude of the loss likely to occur. When 50-microgram portions of bismuth as the pure nitrate were taken through the extraction procedure without regard to re-extracting the aqueous phase in extraction 1, only 86 per cent of the added bismuth was recovered. On the other hand, when the aqueous phase



from extraction 1 was treated as described above, recoveries of 99 per cent were obtained.

An efficient method was adopted for preparing and keeping dithizone solutions. A chloroform-dithizone solution (6 mg. per liter) prepared from purified dithizone and chloroform redistilled and treated with hydroxylamine (1, 7) has been in use intermittently for a period of 6 months without showing signs of deterioration.

Positive findings for the blank determinations shown in Tables II and III are not due to bismuth, but are due partly to errors in density readings and partly to the fact that minute quantities of lead introduced through contamination after extraction 2 have been estimated as bismuth.

Although the analytical results shown in Tables II and III have been obtained with 10-gram samples of blood and 100-ml. samples of urine, the method can be applied to larger or smaller samples, depending upon the concentration of bismuth present and the amount of material available.

### Summary

A photometric "mixed color" dithizone method for the determination of bismuth, applicable to biological material, has been devised. Quantitative extractions are made possible by

isolating the bismuth as the sulfide, interference by other metal sulfides being prevented by complex salt formation with potassium cyanide and specific separation of the bismuth at pH 2.

Although used specifically for the analysis of blood and urine samples, the method is applicable to other materials. It is very sensitive; amounts of bismuth below 5 micrograms can be determined with a high degree of accuracy and 95 per cent recoveries have been obtained for quantities above 50 micrograms.

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## Microidentification of Metrazole in Mixed Aqueous Solutions

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METRAZOLE (cardiazole) has become recognized as a stimulant, and its identification must be of increasing interest to the toxicologist. The literature contains but little information of this nature.

The method of Wollner and Matchett (1, 2) is well adapted for the extraction and separation of alkaloids and other drugs which the toxicologist may encounter in body fluids. Because of its pronounced solubility in water, metrazole is not so readily extracted by this method as the alkaloids, unless appreciable amounts are present. The faintly ammoniacal, aqueous solution is extracted with ethyl acetate in a special extraction device (1) and the solvent is evaporated. The residue is taken up with a few milliliters of chloroform in a special microseparatory tube (2). This solution is extracted first with a small portion of 5 per cent potassium hydroxide and then with 0.5 *N* hydrochloric acid.

Amphoteric alkaloids such as morphine are contained in the alkali extract, strongly basic alkaloids such as strychnine appear in the acid extract, and weakly basic alkaloids such as caffeine remain dissolved in the chloroform. When a small amount of metrazole is present it is found entirely in the chloroform fraction. Traces of metrazole occur in the alkali extract when a considerable amount is present in the original solution. Metrazole is recovered by evaporation of the chloroform, and the residue is taken up in a drop of 0.1 *N* hydrochloric acid on a microscope slide for the microcrystalline test.

Metrazole in very dilute solution fails to form microcrystals with the usual alkaloidal reagents. In more concentrated solutions microcrystals and amorphous precipitates are formed with some reagents. Zwikker (3) has suggested a hydrochloric acid solution of cuprous chloride as a reagent for metrazole, claiming a sensitivity of 1 in 40,000. He prepares this reagent from cupric chloride and sodium sulfite im-

mediately before use, stating that the reagent cannot be preserved.

The author prepares a satisfactory reagent by dissolving cuprous chloride (Baker's) in dilute hydrochloric acid. This operation requires considerably less time than the preparation of Zwikker's reagent. However, this reagent also must be prepared daily, since it is converted rapidly to cupric chloride.

For routine use a 5 per cent solution of cupric chloride in 0.5 *N* hydrochloric acid seems to be much more satisfactory. This reagent is stable and does not have to be prepared daily; furthermore, its sensitivity is comparable to that of cuprous chloride reagent. One drop of a metrazole solution 1 to 1000 (about 50 micrograms) with a drop of the reagent, upon



FIGURE 1. METRAZOLE WITH CUPRIC CHLORIDE REAGENT, DILUTION 1 TO 1000 ( $\times 100$ )



partial spontaneous evaporation, gives an abundance of crystals which are visible even to the naked eye. Even with a metrazole solution so dilute as 1 to 10,000 (about 5 micrograms), a few microcrystals are formed. In these more dilute solutions it is advisable to allow the drop to evaporate completely before examining it under the microscope. Then the addition of a drop of water will dissolve the readily soluble cupric chloride crystals, leaving the well-formed metrazole crystals plainly visible.

The microcrystals are characteristically clusters and rosettes of fine needles, mostly exhibiting arborescent forms resembling a fir tree, and polarizing poorly. Cupric chloride crystals polarize brilliantly and are considerably different in form, so that they scarcely could be confused with metrazole crystals. None of the principal alkaloids or other common drugs which the author has tested with cupric chloride reagent gave microcrystals which might be confused with metrazole. These alkaloids in mixed aqueous solution with metrazole did not appreciably inhibit its separation and identification.

For obvious reasons the results of animal experimentation and data on the mode of elimination of metrazole cannot be made public at the present time.

### Modified Method of Wollner and Matchett

**SEPARATION AND IDENTIFICATION OF METRAZOLE IN BODY FLUIDS.** Small amounts (1.0, 0.5, 0.1, and 0.05 mg.) of metrazole were added to 100-ml. samples of body fluids (and washings). Twenty-five grams of ammonium sulfate, c. p., were dissolved in each sample (2), and the solution was made faintly ammoniacal to litmus paper. The solution was then extracted with ethyl acetate in the special extraction device (1), and the solvent was filtered and evaporated to dryness on the steam bath.

The residue was taken up by washing repeatedly with small portions of chloroform (total volume about 3 ml.) and trans-

ferred to a microseparatory tube (2) by means of a medicine dropper. A 0.25-ml. portion of 5 per cent potassium hydroxide was added to the tube, which then was shaken about 6 minutes in a blood pipet shaker, and centrifuged, and the alkali layer was removed to a second tube by means of a Wright pipet. This alkali extraction was repeated once. Then the chloroform solution was extracted with 0.5 ml. of 0.5 *N* hydrochloric acid by shaking 2 minutes, centrifuging, and transferring the acid layer to a third tube. The acid extraction was repeated once with 0.25 ml. of 0.5 *N* hydrochloric acid, and the chloroform solution was filtered and evaporated to dryness on the steam bath. The residue was taken up in one drop of 0.1 *N* hydrochloric acid and transferred to a microscope slide and one drop of the cupric chloride reagent was added to it.

Microcrystals were formed in the three samples which contained 1.0, 0.5, and 0.1 mg. of metrazole, but not in the sample which contained 0.05 mg. Therefore, the smallest amount of unchanged metrazole which can be extracted and identified by this method is about 0.1 mg. (100 micrograms) per 100 ml.

### Summary

A toxicological method for the extraction and separation of metrazole from mixed aqueous solutions with other drugs is described, which is capable of extracting and identifying 0.1 mg. of metrazole in 100 ml. of aqueous solution. Cupric chloride is suggested as a reagent for the detection and identification of metrazole. The sensitivity is 1 part in 10,000.

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## A Microbiological Assay for Riboflavin

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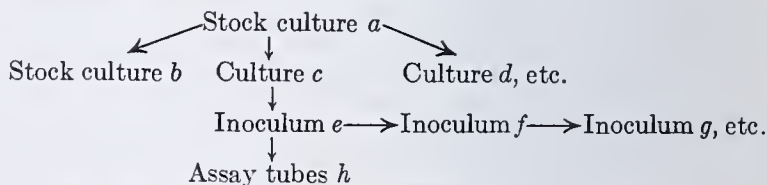
IN A recent critical article, Ellinger (5) discussed the errors involved in the chemical and physicochemical methods for the quantitative estimation of riboflavin in biological products, concluding that at present biological assay provides the most reliable method for the estimation of this vitamin. The disadvantages of current biological methods for riboflavin are common knowledge. They are expensive, time-consuming, and have limited applicability because of the quantities of material required for assay. In addition, the reliability and accuracy of such assays are open to question (3). For example, the value of the Bourquin-Sherman unit (3) in terms of pure riboflavin as reported in the literature (or as it may be estimated from data in various papers) varies from less than 2 to approximately 5 micrograms per unit (1, 2, 9, 14).

In previous papers (16, 17) riboflavin was shown to be essential for the growth of certain lactic acid bacteria, and the amount of growth was found in some cases to be directly proportional to the concentration of riboflavin in the culture medium. The growth-promoting activity of various isomers and homologs of riboflavin was also determined (16). The naturally occurring substance proved more active than any of the synthetic variants, while degradation products produced from riboflavin by light were completely inactive.

The present paper describes an assay method for riboflavin in natural materials, which has been developed on the basis of the above information.

### Stock Culture and Inoculum

The organism used for assay purposes is carried in this laboratory as *Lactobacillus casei*; it is probably identical with the *Bacillus casei*  $\epsilon$  of Freudenreich (8). The requirement of this organism for riboflavin and other growth factors has been previously described (17, 18). Stab cultures of the organism are carried in yeast-water agar containing 1 per cent of glucose. The method of preparing and carrying cultures is indicated in the following diagram:



From the original culture, *a*, a series of stab transfers (*b*, *c*, *d*, etc.) are made into yeast water-glucose agar. After 24 hours' incubation at 37° C. these are stored in the refrigerator. At least one tube, *b*, is reserved as the stock culture. The other tubes (*c*, *d*, etc.) may be used to prepare inoculum as described below. If assays are to be made on each of several successive days, one need not grow inoculum from stock cultures (*c*, *d*) each day, but can transfer a drop of inoculum *e* to a similar tube, *f*, which is incubated for use the next day. Inoculum cultures should not be used after they are more than 36 hours old. One should return to a stock culture about every 5 days to minimize chances of contamination and of bacterial variation. New stock cultures corresponding to *b*, *c*, and *d* are prepared at monthly intervals from a tube such as *b* of the preceding month.



### Basal Medium

The riboflavin-free basal medium used is a modification of that developed in previous studies (16, 17). It contains photolyzed, sodium hydroxide-treated peptone, 0.5 per cent; glucose, 1 per cent; sodium acetate, 0.6 per cent; cystine,

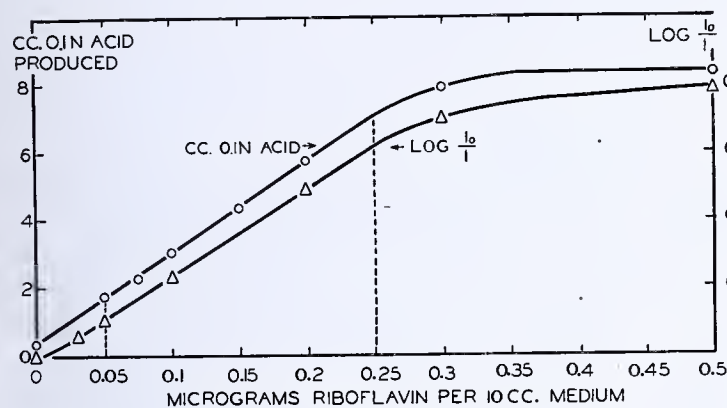


FIGURE 1. RESPONSE OF *L. casei* TO PURE RIBOFLAVIN

0.01 per cent; inorganic salts; and riboflavin-free yeast supplement equivalent to 0.1 per cent yeast extract. The constituents are prepared and kept as follows:

**PHOTOLYZED, SODIUM HYDROXIDE-TREATED PEPTONE.** A mixture of 40 grams of peptone (Difco Bacto) in 250 cc. of water and 20 grams of sodium hydroxide in 250 cc. of water is exposed in a 25-cm. crystallizing dish to light from a 100-watt bulb with reflector at a distance of approximately 30 cm. for 6 to 10 hours, and is then allowed to stand at room temperature for an additional 18 to 14 hours (24 hours in all). The sodium hydroxide is neutralized with glacial acetic acid (27.9 cc.), 7 grams of anhydrous sodium acetate are added, and the mixture is diluted to 800 cc. This solution contains the equivalent of 5 per cent of peptone and 6 per cent of sodium acetate, which is ten times the concentration of these materials in the final medium. It is preserved under toluene. The above treatment destroys other substances (18) besides riboflavin which are essential for growth of the assay organism. These are supplied in the yeast supplement.

**YEAST SUPPLEMENT.** To a solution of 100 grams of Bacto-yeast extract in 500 cc. of water 150 grams of basic lead acetate (Horne's sugar reagent) dissolved in 500 cc. of water are added, and the precipitate is filtered off. (This yeast extract consists of dry matter from a clarified water extract of autolyzed yeast and is prepared for use in bacteriological culture media. It may be obtained from the Difco Laboratories, Inc., Detroit, Mich.) Ammonium hydroxide is added to a pH of about 10.0, and the precipitate formed is again filtered off. The filtrate is just acidified with glacial acetic acid, the excess lead precipitated with hydrogen sulfide, and the lead sulfide filtered off and discarded. All the riboflavin is removed by this treatment. The filtrate is made to a volume of 1000 cc., and stored under toluene in the refrigerator. One cubic centimeter of this preparation is equivalent to 100 mg. of the original yeast extract.

**INORGANIC SALTS.** Solution A consists of 25 grams of potassium hydrogen phosphate and 25 grams potassium dihydrogen phosphate dissolved in 250 cc. of water. Solution B consists of 10 grams of magnesium sulfate heptahydrate, 0.5 gram of sodium chloride, 0.5 gram of ferrous sulfate heptahydrate, and 0.5 gram of manganese sulfate tetrahydrate dissolved in 250 cc. of water. Five cubic centimeters of solution A plus 5 cc. of solution B contain inorganic salts for 1000 cc. of basal medium.

**CYSTINE.** A solution of cystine hydrochloride containing 1 mg. of cystine per cc. is prepared, and kept under toluene.

### Standard Riboflavin Solutions

For a stock solution, pure crystalline riboflavin is accurately weighed and dissolved in warm 0.02 *N* acetic acid. A convenient concentration is 100 micrograms per cc. This solution is kept in the refrigerator under toluene. For use from day to day, a more dilute solution (10 micrograms per cc.) is prepared from the stock solution by dilution with 0.02 *N* acetic acid. [Synthetic *D*-riboflavin of at least 99 per cent

purity (Merck and Company, Inc.) was used as the primary standard throughout this investigation.]

### Procedure

The fermentations are carried out in ordinary chemical or bacteriological test tubes (16 × 150 mm. to 20 × 150 mm.). A metal or wire rack which holds each tube separately and upright and which can be autoclaved without damage is very convenient, but not necessary if the tubes are properly marked. If 50 assay tubes are to be set up from stock solutions of the above concentrations, 50 cc. of photolyzed, sodium hydroxide-treated peptone solution, 50 cc. of cystine hydrochloride solution, 5.0 cc. of yeast supplement, 5.0 grams of glucose, 2.5 cc. of solution A, and 2.5 cc. of solution B are mixed, the pH is adjusted to 6.6 to 6.8 with sodium hydroxide, and the mixture is diluted to 250 cc. Five cubic centimeters are pipetted into each of the 50 tubes, and a suitable aliquot of the riboflavin-containing extract is added. The contents of each tube are then diluted, where necessary, to give a total volume of 10 cc. Thus as much as 5 cc. of liquid may be added with the sample. The volumes indicated should be measured with an accuracy of ±0.1 cc. The tubes are plugged with cotton, sterilized in the autoclave at 1 kg. per sq. cm. (15 pounds per sq. inch) pressure for 15 minutes, and allowed to cool. The tubes are then ready for inoculation.

### Inoculation and Incubation

For inoculum, a stab from a stock culture is made into a sterile tube of basal medium to which has been added 0.5 to 1.0 microgram of riboflavin per 10 cc. The culture is incubated 24 hours at 37°, and the cells are centrifuged out aseptically and resuspended in an equal volume of sterile 0.9 per cent sodium chloride solution. One drop (ca. 0.05 cc.) of this suspension is used to inoculate each assay tube. The inoculated assay tubes are incubated at 37° to 40° C. for 1 to 3 days.

### Standard Curve

With each set of assays there are set up duplicate tubes containing, per 10 cc. of medium, 0.0, 0.05, 0.075, 0.1, 0.15, 0.2, and single tubes containing 0.3 and 0.5 microgram of riboflavin. Titrations or growth data secured from these tubes allow the construction of a standard curve (Figure 1).

### Determination of Bacterial Response

Two methods have been used to determine quantitatively the response to added riboflavin. The first involves measurement of the turbidity produced by the growth of the organism.

The Evelyn photoelectric colorimeter (?) has been employed for this purpose with excellent results, using the 540 mμ filter. The galvanometer is adjusted to read 100 with the uninoculated basal medium in the colorimeter tube. The assay tubes are well shaken to suspend all bacterial cells uniformly; medium and cells are then transferred to the colorimeter tube and the percentage of incident light transmitted is read directly from the galvanometer. Overhead lights must be off while such readings are being made to prevent stray light from being reflected into the photoelectric cell by the turbid suspension.

This procedure cannot be used when turbid or highly colored extracts are being assayed for their riboflavin content. Corrections for the turbidity of extracts added are not generally valid, since the turbidity is frequently altered by the acid produced during the growth of the organism.

In the second method, which is of general applicability, the acid produced during growth is measured. Contents of the assay tubes are transferred to a 125-cc. Erlenmeyer flask with 10 to 20 cc. of distilled water and titrated to pH 6.8 to 7.0 with 0.1 *N* sodium hydroxide. Bromothymol blue is a satisfactory indicator. A color-comparison flask aids in recognition of the end point, which is reproducible to ± 0.1 cc.

### Period of Incubation

Turbidity of cultures grown in the basal medium here described reaches a maximum in approximately 24 hours, remains constant for about 48 hours, and then slowly de-



creases. Turbidity measurements are therefore best made at the end of 24 hours. Acid production, however, increases steadily for 3 to 4 days, so that the method is more sensitive if the cultures are titrated after the longer interval. However, practically the same results are secured when shorter incubation times are used. In the work described below acid production has been measured after 72 hours' incubation except where otherwise stated.

Evaluation of Bacterial Response in Terms of Riboflavin

The response of the organism to pure riboflavin in a typical fermentation is shown in Figure 1. The turbidity measurements were made after 24 hours' incubation. Since within a limited range turbidity and acid production are directly proportional to the concentration of riboflavin, the response elicited by an unknown sample can be evaluated in terms of riboflavin by interpolation on the standard curve. To yield valid results the riboflavin content of the assay cultures must fall on the straight-line portion of the curve above 0.05 microgram per 10 cc.—i. e., between 0.05 and 0.25 microgram per 10 cc. in Figure 1. Preferably each sample should be assayed at three levels which fall within this range with duplicate tubes at each level. The values obtained at the three levels are averaged for the final result.

The results of assays of "unknown" solutions of pure riboflavin by this method are shown in Table I. Similar results have been obtained by several independent observers in this laboratory. No difficulty is experienced in determining to  $\pm 5$  per cent even a few hundredths of a microgram of riboflavin per cubic centimeter when pure solutions are being analyzed.

TABLE I. RECOVERY EXPERIMENTS WITH PURE RIBOFLAVIN

Acidimetric Assay			Turbidimetric Assay		
Riboflavin present	Riboflavin found	Recovery	Riboflavin present	Riboflavin found	Recovery
Micrograms/cc.	Micrograms/cc.	%	Micrograms/cc.	Micrograms/cc.	%
0.0198	0.0201	101.5	0.013	0.013	100
0.071	0.074	104.2	0.064	0.063	98.4
0.252	0.251	99.6	0.236	0.225	95.5
0.672	0.685	101.9	0.55	0.59	107.0
2.20	2.10	95.5	1.97	2.00	101.5

Applications to Natural Products

For extraction of riboflavin from natural products autoclaving the finely divided material at 1 kg. per sq. cm. (15 lb. per sq. in.) pressure for 15 minutes with a large volume of water is recommended. Extraction with boiling 0.1 *N* hydrochloric acid and subsequent neutralization are also effective. In the latter case not more than 50 mg. of sodium chloride should be added to the assay tubes with the aliquot to be analyzed. Amounts greater than this first increase, then decrease the response of the test organism to a given quantity of riboflavin. It was demonstrated in separate experiments that the biological potency of a dilute solution of riboflavin in 0.1 *N* hydrochloric acid was not detectably affected by autoclaving at 1 kg. per sq. cm. (15 lb. per sq. in.) pressure for 30 minutes.

Several lines of evidence have been used to guard against possible interfering substances:

Assays are made at different levels, and only those assays which give concordant results at the different levels are regarded as reliable.  
Recoveries of known quantities of pure riboflavin in the presence of the natural material have been made.

TABLE II. RIBOFLAVIN ASSAYS ON MILK AND LIVER

Sample	Amount Assayed <sup>a</sup>	Riboflavin Added per Gram Sample	Riboflavin Found Per tube	Riboflavin Found Per gram sample	Recovery of Added Riboflavin
	Mg.	Micrograms	Microgram	Micrograms	%
Milk A	50	None	0.097	1.94	
	60	None	0.126	2.10	
	75	None	0.146	1.95	
				Av. 2.00	
	17	1.76	0.062	3.64	
	25.5	1.76	0.094	3.68	
Milk B	34	1.76	0.132	3.88	
				Av. 3.70	97
	50	None	0.081	1.61	
	60	None	0.100	1.68	
	75	None	0.136	1.81	
				Av. 1.69	
Fresh beef liver	17	1.76	0.061	3.58	
	25.5	1.76	0.092	3.60	
	34.0	1.76	0.124	3.65	
				Av. 3.61	109
	2.01	None	0.082	41.0	
	3.02	None	0.134	44.6	
Photolyzed milk serum	4.02	None	0.172	42.8	
	6.03	None	0.241	40.2	
				Av. 42.2	
	1.02	24.4	0.070	68.6	
	1.54	24.4	0.100	65.0	
	2.04	24.4	0.146	71.5	
Photolyzed liver extract	3.08	24.4	0.214	69.5	
				Av. 68.6	108
	100	None	0.00	0.00	
	200	None	0.00	0.00	
	200	0.50	0.10	0.50	100
	200	0.75	0.15	0.75	100
Photolyzed liver extract	2.4	None	0.00	0.00	
	2.4	41.6	0.095	39.6	95
	2.4	62.5	0.148	61.6	98.7
	3.2	None	0.00	0.00	
	3.2	31.3	0.100	31.3	100
	3.2	46.9	0.155	48.5	103

<sup>a</sup> Expressed in terms of weight of the original sample.

The riboflavin in various extracts has been destroyed by the least drastic and most selective method available—namely, by the action of visible light on the extract at pH approximately 7.0—and recoveries of pure riboflavin in the presence of the photolyzed material have been made.

Assays have been made on samples which have also been assayed for riboflavin by other biological methods, and the results compared.

The sensitivity of the organism to inhibition by various reagents has been investigated.

Most of this evidence was collected in connection with assays on samples of milk, liver, and yeast.

The data presented in Table II indicate that the apparent riboflavin contents of milk and liver samples as determined at different levels were satisfactorily constant, and that added riboflavin was recovered with an error of 10 per cent or less. The milk was diluted with distilled water and aliquots equivalent to the amounts indicated were added directly to the assay tubes. The milk serum was prepared by making the milks lightly acid with acetic acid, warming briefly to 80° to 90° C. and filtering. The clear serum was photolyzed by readjusting to pH 7.0, adding a few drops of chloroform as a preservative, and exposing a 0.5-cm. layer of the solution for 24 hours at room temperature (25° or less) to the light from a 100-watt bulb with reflector at a distance of 25 cm. Sufficient water approximately to balance evaporation was added during the photolysis, and the final solution was diluted accurately to the original volume.

The liver was ground and divided into two parts and the riboflavin to be recovered was mixed into one portion. The samples were then extracted by boiling for 5 minutes with 3 volumes of 0.1 *N* hydrochloric acid, and the residues were centrifuged off and re-extracted twice by the same procedure.



The turbid extracts were neutralized and suitable aliquots taken for assay. The photolysis was carried out as above described on a portion of the neutralized extract from which insoluble matter had been removed by centrifuging.

The results of microbiological and rat assays on the same samples of various materials are summarized in Table III. Extracts for the bacterial assay were prepared by autoclaving

TABLE III. COMPARATIVE RIBOFLAVIN ASSAYS OF NATURAL PRODUCTS

Material	Riboflavin Content <sup>a</sup>			
	Microbiological Assay		Rat Assay	
	Direct	Extract		Bourquin-Sherman units
	Micro-grams	Micro-grams	Micrograms	
Dried grasses				
Sample I	...	24.4	20.0	..
Sample II	...	24.1	25.0	..
Sample III	...	22.6	22.0	..
Sample IV	...	23.9	20.0	..
Dried oat plant	30.3	31.2	35.0	..
Skim-milk powder	17.1	..	17.0	..
Debittered yeast a	39.2	38.5	37	..
Debittered yeast b	...	36.5	(38.8)	17.7
Debittered yeast c	34.7	33.6	(34.4)	15.7
Yeast extract	149.6	..	(145.6)	66.5
Nondebittered yeast	31.8	32.8	(32.0)	14.6

<sup>a</sup> Per gram dry weight.

the weighed sample with 100 times its weight of water at 1 kg. per sq. cm. (15 lb. per sq. in.) pressure for 15 minutes. The extract and residue were then diluted to a volume of 100 cc. for each gram of sample taken, solid material was removed by centrifugation, and an aliquot was assayed for the riboflavin content. In some cases, as indicated in Table III, the suspension was assayed directly. The average value for the Bourquin-Sherman unit calculated from these data is 2.19 micrograms per unit. The values for the riboflavin content of yeast samples given in parentheses in column four were calculated from the Bourquin-Sherman units with this factor.

The data presented in Table IV indicate roughly the sensitivity of *L. casei* to a number of miscellaneous materials. These results indicate that the organism is resistant to a variety of toxic materials in concentrations higher than those ordinarily encountered in biological extracts.

TABLE IV. SENSITIVITY OF *Lactobacillus casei* TO INHIBITION BY VARIOUS SUBSTANCES

Substance Tested	Concentration Micrograms/cc.	Extent of Inhibition
Cu <sup>+++</sup>	40	Complete
Cu <sup>++</sup>	20	Just noticeable
Mn <sup>++</sup>	40	None
Fe <sup>+++</sup>	40	None
Zn <sup>++</sup>	40	None
Ba <sup>++</sup>	50	Just noticeable
Pyridine	500	None
Ethanol	2,000	None
Methanol	2,000	None
KCl	1,000	None
NaCl	20,000	None

<sup>a</sup> Cu, Mn, Fe, and Zn were tested in the form of the sulfates; Ba as the chloride.

Riboflavin Content of Various Biological Materials

The riboflavin content of several natural products as determined by the present method is compared in Table V with values given by other investigators for similar products. Where several samples have been analyzed, the range obtained is given. Assays on milk, milk serum, skim-milk powder, dried whey, egg white, and egg yolk were made directly. A hydrochloric acid extract of the beef liver and soybean meal was assayed, while the extract for assay of the dried pork liver was obtained by autoclaving with water and centrifuging off the insoluble residue.

TABLE V. RIBOFLAVIN CONTENT OF BIOLOGICAL MATERIALS

Material	Micro- biological Assay	Literature Values	Method of Assay	Reference
<i>Micrograms per gram</i>				
Beef liver, fresh	44.0	35.6	Colorimetric	4
		15-17	Photometric	13
Rat liver, fresh	34.0	15-17	Photometric	13
Pork liver, vac- uum-dried	92-104	100	Chick	15
Liver meal, com- mercial	50.0	...	.....	..
Whole milk	1.5-2.5	1.7-2.4	Rat	12
		1.0-1.5	Fluorimetric	10
Milk serum	1.3-1.9	...	.....	..
Dried whey	23	30	Chick	15
Skim-milk pow- der	17	20	Chick	15
Soybean meal	3.0	3.0	Chick	15
Egg white, fresh	3.1	4-5	Colorimetric	6
Egg yolk, fresh	7.6	5-6	Colorimetric	6

Constancy of Assay Results

The degree of constancy which may be expected when assays are run on the same product at different times is indicated in Table VI. The second assay was made 2 weeks after the first. The maximum difference is about 8 per cent.

TABLE VI. CONSTANCY OF ASSAY RESULTS

Sample	Riboflavin Content	
	Assay 1	Assay 2
	Micrograms per gram	
Beef liver, fresh	42.2	45.7
Rat liver a, fresh	33.0	31.2
Rat liver b, fresh	36.9	34.3
Skim-milk powder	17.0	17.2

Discussion

RELIABILITY OF THE METHOD. From the results reported in this and previous papers it is evident that riboflavin is indispensable for growth of *L. casei*. A growth response caused by the addition of any material to the riboflavin-free basal medium may therefore be regarded as a reliable qualitative indication of the presence of riboflavin in that material. The high degree of structural specificity required for activity (16), the identity of all flavins so far isolated from natural sources (11), and the complete inactivity of photolyzed extracts of biological materials (cf. Table II) strongly support this view.

While it has unfortunately not been possible as yet to test such substances as riboflavin phosphate and Warburg's flavin-adenine dinucleotide (19), it is very probable that the bacteria respond not only to free but also to the various combined forms of riboflavin. Thus several materials, such as yeast and liver, which are known to contain most of their riboflavin in combined forms, give values by the bacterial assay which are as high or higher than those found by several other methods.

The reliability of the response as a quantitative measure of riboflavin and riboflavin only is more difficult to establish, since inhibition or stimulation of the organism by substances introduced with the sample to be assayed is possible. The question of inhibition seems to be satisfactorily settled by the data in Table IV, by the successful recovery of pure riboflavin added to the sample, and particularly by the recovery of riboflavin in the presence of photolyzed extracts, which would presumably still contain any inhibitory substances originally present.

Stimulation of the organism, which would produce falsely high values for riboflavin, might conceivably result from the presence of food materials or of unknown growth factors in the sample. The former possibility seems remote in view of analyses of known amounts of riboflavin which were carried out with a medium containing twice the usual amount of



glucose and peptone. The apparent riboflavin content was increased less than 10 per cent by the extra food materials available to the organism.

Since the addition of a single pure substance, riboflavin, to the basal medium permits growth through repeated subculture (16), it follows that the medium so supplemented contains all the accessory growth factors essential for *L. casei*. The possible existence of other nonessential but stimulatory substances which are not supplied with the yeast supplement cannot be overlooked. The assumption has been made in the above work that the effect on growth of such stimulatory factors will be negligible in a medium which contains suboptimal quantities of an essential growth factor (riboflavin). The validity of this assumption is supported by the quantitative recovery of pure riboflavin in the photolyzed and unphotolyzed extracts as described above. In each case the amount of photolyzed material used was comparable to the amount of the original sample required for the assay. The destruction of stimulatory substances other than riboflavin during photolysis, although possible, appears unlikely in view of the mild conditions employed.

The comparative assays summarized in Table III offer additional support for the reliability of the bacterial method, although the questionable accuracy of the rat assay makes it difficult to evaluate such evidence. Few critical tests of the specificity of the rat or chick assay method for riboflavin have been made.

**SOURCES OF ERROR.** The presence in the assay tube of large amounts of solid material from the substance being assayed affects the assay adversely. Thus when recoveries of pure riboflavin were attempted in the presence of the residue from the hydrochloric acid extraction of liver described above the results were high and variable, although the residue alone showed a riboflavin content of zero. Similarly, if substances naturally low in riboflavin, such as the cereal grains, are added directly (after grinding) to the medium for assay, the riboflavin contents calculated from the different levels do not agree. Thus in these cases one must resort to extraction. Obviously, too, the smaller the riboflavin content of a substance, the more extract must be added in order to obtain sufficient riboflavin to fall within the specified range, with the consequent addition of larger amounts of extraneous substances which may affect the assay result. In cases, therefore, where assays at different levels do not check closely enough, or where recoveries of added riboflavin are seriously in error, further purification of the extract assayed is indicated.

On the other hand, incorporation of inert solid material such as Filtercel in the medium did not affect the recovery of added riboflavin. Similarly, the small amount of solid material added in the assay of milk and milk products apparently did not interfere, since accurate recoveries of added riboflavin were obtained in the presence of such material.

The method requires the maintenance of a pure culture of *L. casei*. Contamination of the assay tubes with other microorganisms produces false results through riboflavin synthesis and associated growth phenomena.

**USEFULNESS OF THE METHOD.** The assay is applicable to crude extracts or in some cases to the whole ground sample, so that extensive preliminary purification with attendant losses of riboflavin is unnecessary. It requires very small amounts of sample, no elaborate or unusual equipment, and is relatively rapid. Routine analyses now under way in this laboratory have shown that one operator can conveniently carry out 15 to 20 assays per working day. The accuracy of the method is of the order of  $\pm 10$  per cent.

### Summary

A biological assay for riboflavin, which is based on the essential nature of this substance for the growth of *Lacto-*

*bacillus casei*, is described. The reliability of the method is supported by agreement of the assay results at different levels, recovery of added riboflavin, successful determination of riboflavin in the presence of photolyzed extracts, and specificity of structure required for activity.

The results compare well with other bioassays for riboflavin on the same products. The method is rapid, and requires only very small amounts of sample.

### Acknowledgment

The authors wish to thank Dr. Levene of the Premier-Pabst Corporation, Milwaukee, for supplying the yeast samples with the rat assay results given in Table III. The rat assays on the other samples were carried out by Professor Elvehjem and Mr. Wagner, to whom the authors also wish to express their thanks.

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**CORRECTION.** In the article on "Analytical Balances in Quantitative Microanalysis" [IND. ENG. CHEM., Anal. Ed., **11**, 226 (1939)] the following corrections should be made:

In Table I  $\frac{100}{P}$  should read  $\frac{1000 f}{P}$ .

In Equation 9, substitute "P" for "M".

The last two items in Table II should read as follows:

	G./l.	f	Cu. mm.	Cu. mm.
Cl as AgCl in sea water	20	0.247	75	190
P as phosphomolybdate in serum	0.2	0.016	480	1200

A. A. BENEDETTI-PICHLER



# A Modified Buret for Microanalysis of Gases

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IN USING the method for the microanalysis of gases described by Blacet and Leighton (1), the author experienced considerable difficulty because of the tendency of the mercury levels to drift up or down the capillary buret during the time required to take the readings. A method of avoiding this difficulty has been described by Blacet, MacDonald, and Leighton (2), but an alternative method, used in this laboratory, has proved to have valuable additional advantages.

The drift in the mercury levels is evidently due to the fact that a small displacement of the upper level downward, for example, causes a marked increase in the pressure of the gas and of the pressure of the mercury in the rubber pouch at the base of the buret. This increased pressure makes the gas contract and the rubber pouch distend, both of which cause the upper mercury level to move downward again. If the rubber is not sufficiently stiff, the sample of gas may even be lost into the base of the buret in this manner.

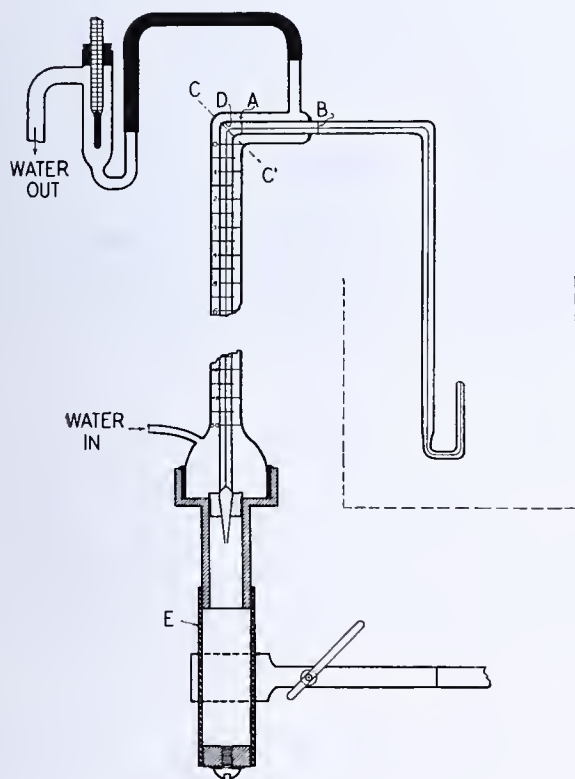


FIGURE 1. DIAGRAM OF BURET

This difficulty may be readily overcome by maintaining the upper mercury level in a horizontal rather than a vertical capillary tube. The same principle has been employed in a different manner in an apparatus described by Swearingen, Gerbes, and Ellis (3).

A simple method which does not occupy an undue amount of space is shown in Figure 1, which is similar to the buret described by Blacet and Leighton except that the water jacket now follows the capillary tube up and over the bend at the top. The water jacket is made from a Pyrex buret sealed at the two ends with picene wax (not with de Khotinsky cement, since this slowly disintegrates under water). The capillary tube which runs through the buret is placed near the front surface of the buret, rather than centered, so that the lower mercury level can be read from the buret graduations without danger of serious paral-

lax errors. Two lines, A and B in Figure 1, are marked on the horizontal portion of the capillary, one close to the bend, the other close to the end of the water jacket. It is convenient to choose positions for these marks such that the volume of the capillary between the marks and the zero of the buret is an integral number of the units of volume employed. This may be readily accomplished if the apparatus is calibrated after assembly but before the horizontal arm of the water jacket is sealed on at C-C'.

Readings are taken by drawing the gas into the buret in the manner described by Blacet and Leighton and adjusting the upper level to coincide with A or B. The lower mercury level is read from the graduations on the buret. Water from a large vessel is circulated through the water jacket. Since its temperature never deviates largely from room temperature, no appreciable error arises from the fact that a small fraction of the gas extends beyond the end of the water jacket when B is used. This arrangement has been adopted to relieve the operator from eyestrain during the adjustments. For measuring very small volumes of gas (less than about 20 cu. mm.) A must, of course, be used. The temperature of the water in the water jacket is conveniently read from the thermometer arranged as in Figure 1.

In a buret of this type the mercury shows no tendency whatsoever to drift in the manner described. If the mercury in the movable cup (shown by dotted lines) is always brought to a fixed level when a reading is to be made, the pressure on the sample of gas will be the same in consecutive readings unless large barometric changes have occurred. The time required for most analyses is short enough to permit one to ignore entirely all pressure corrections, which is a considerable simplification over the procedure ordinarily followed.

A marked advantage of this type of buret is that it can be cleaned without being dismantled. The "scum" carried into the buret is carried by the upper mercury thread, and since this is not ordinarily drawn into the vertical portion of the capillary tube, only the horizontal portion requires cleaning. To clean the buret the mercury cup is removed and a beaker containing a cleaning solution of potassium dichromate and concentrated sulfuric acid is put in its place. Before the tip of the buret is submerged in the solution, however, the mercury in the buret is drawn back until the level of the thread is about 10 cm. below the bend, D. The cleaning solution is then drawn into the buret up to D but no farther. After several hours the acid is expelled and distilled water is drawn up in its place. The buret is dried after several such rinsings by evacuating the capillary, an operation which must be done with some care to avoid drawing mercury into the horizontal tube.

Minor advantages of the buret here described are that only one reading is taken from the calibration curve for each measurement and that the volume may be recorded directly without taking differences.

## Summary

A modification of the Blacet-Leighton gas microburet is described. The mercury threads are easily adjusted and do not drift from their set positions. Corrections for pressure are not ordinarily required. The buret may be cleaned without dismantling.

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# MODERN

# LABORATORIES



## BAGLEY HALL, UNIVERSITY OF WASHINGTON

W. L. BEUSCHLEIN, University of Washington, Seattle, Wash.

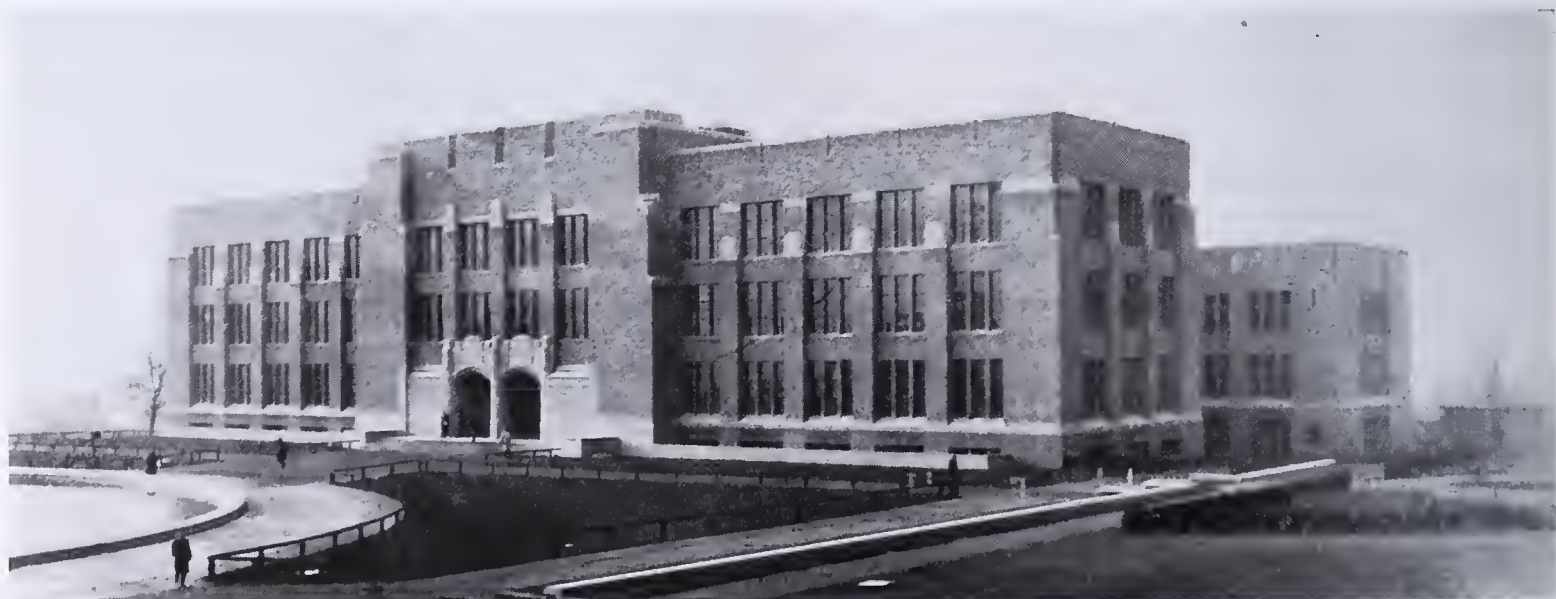
**D**ANIEL Bagley Hall at the University of Washington houses the Department of Chemistry and Chemical Engineering and the College of Pharmacy. Funds for the construction, amounting to \$1,250,000, were supplied by state and federal grants. The structure has three and one-half floors with four wings, the over-all dimensions being  $260 \times 380$  feet. Approximately one acre of ground area is covered, the total volume being 2,400,000 cubic feet. The cost has been estimated at 52 cents per cubic foot.

A study of the requirements of a new building under the supervision of S. G. Powell and the author had provided fundamental designs of general laboratory space when funds were allocated for construction. All designs, plans, and acceptances of bids were completed within the ninety days specified under terms of the federal grant. The information presented in the publication of the National Research Council, "Construction and Equipment of Chemical Laboratories", was of great value, as was also a joint report by Carl F. Gould and H. K. Benson on the inspection of eleven recently constructed laboratories in the United States. Special assistance was rendered by Professor Hoover of Wesleyan University and Dr. Coleman of Mellon Institute. The plans and specifications were prepared by F. A. Naramore and Granger and Thomas, associate architects.

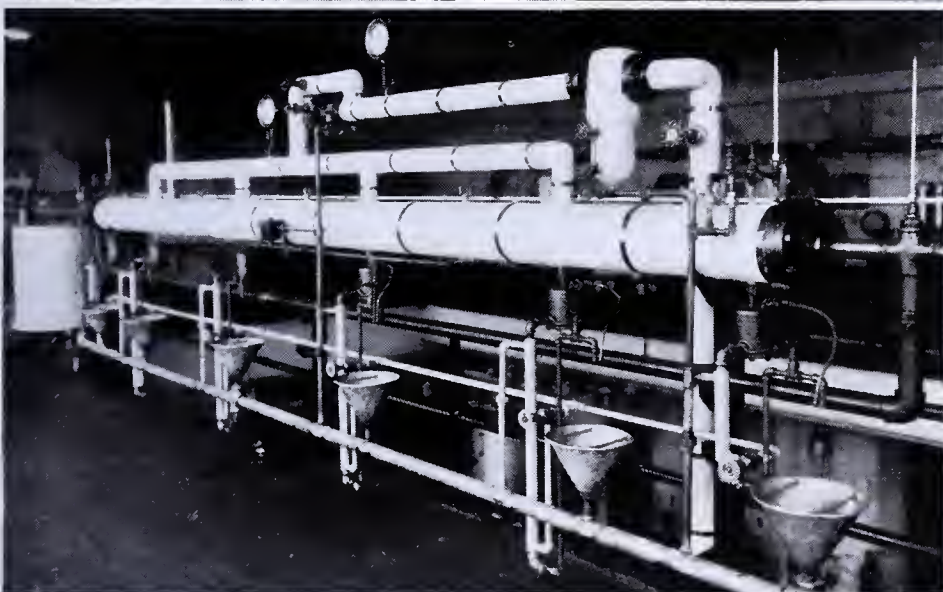
THE building is of reinforced concrete construction and surfaced outside with brick. Partitions are of hollow tile, and those forming laboratory walls are to remain unpainted.

All laboratories have access to natural lighting, the inner volume of the structure being utilized for corridors, lecture rooms, and storage. A subbasement contains the mechanical equipment, such as air washers and conditioners, ventilation fans, heaters, steam distributors, and reducing valves. The space above the third floor is used for fume ducts, fans, and water-distillation equipment.

The areas enclosed by the inner corridors have been given over to stock storage, dispensing, and lecture rooms. A volume of 150,000 cubic feet has been provided for general storage and dispensing rooms. The service division has a small reconditioning room equipped with the usual facilities, including paint gun, buffing wheel, and soaking tanks. That division also has charge of the refrigeration plant, distilled water, hydrogen sulfide, and variable voltage supply. The refrigeration plant supplies ice for the boxes on the various floors, sharp and normal refrigeration to the biochemistry laboratory, and cooling coils for the unit operations laboratory. Hydrogen sulfide is delivered from the cylinders to manifolds at reduced pressures into iron pipes for use in general chemistry. Electrical energy is brought to the laboratory at 2300 volts alternating current and is transformed to 120 and 208 volts for lighting and the usual motors and heaters. Variable-voltage transformers for alternating current and generators and batteries for direct current located in the electrical supply room are under the supervision of the service division. The Barnstead still delivers 10 gallons per hour of distilled water to a 270-gallon aluminum storage







Upper left. ONE OF FOUR ANIMAL ROOMS.  
KEYHOLE STANDARDS USED FOR SHELVING

Upper right. TYPICAL RESEARCH LABORATORY

Left. UNIT OPERATIONS LABORATORY.  
STEAM TO LIQUID HEAT EXCHANGE

tank from which distribution is made through aluminum pipe and valves, the latter having silver seats.

Eight lecture rooms containing a total of approximately 840 seats are available. The arrangement of the two larger rooms with the adjoining supply room for lecture table experiment equipment is working very nicely. The large lecture hall has a soundproof booth with sound and silent projectors, multiplex controls at the lecturer's station, and down-draft hood on the lecture bench; 3 per cent of the chairs are for left-handed students.

Rooms for graduate research were designed to be occupied by two to four persons. The distribution of these rooms about the building has permitted an economical use of floor space. Facilities available in such rooms include compressed air, oxygen, 15 kw. of 120- to 208-volt 60-cycle alternating current, variable-voltage (0 to 400) alternating and (0 to 150) direct currents, in addition to hot and cold water, gas, steam, fume hood, and fire protection. Vibrationless piers have been installed in some rooms.

Some interesting features were developed in the arrangement of the analytical laboratories. A centrally located room equipped with ball mills, power-driven sieves, and dividers furnishes space for the preparation, storage, and indexing of the 63,000 unknowns carried by this division. The wide corridor connecting the two main analytical laboratories is used for the work in electrolysis. Each laboratory is provided with a Kjeldahl room of 144 digestion capacity.

The chemical engineering laboratories contain small- and large-scale equipment for the study of unit operations, unit processes, and technical analysis of industrial materials.

The primary services in these rooms furnish steam up to pressures of 175 pounds per square inch, 3-phase 60-cycle alternating current up to 400 amperes at 208 volts, variable-voltage direct current up to 150 amperes, gas, water, compressed air, and fume ducts, so that semiplant equipment can be operated. A machine shop is operated in conjunction with this division.

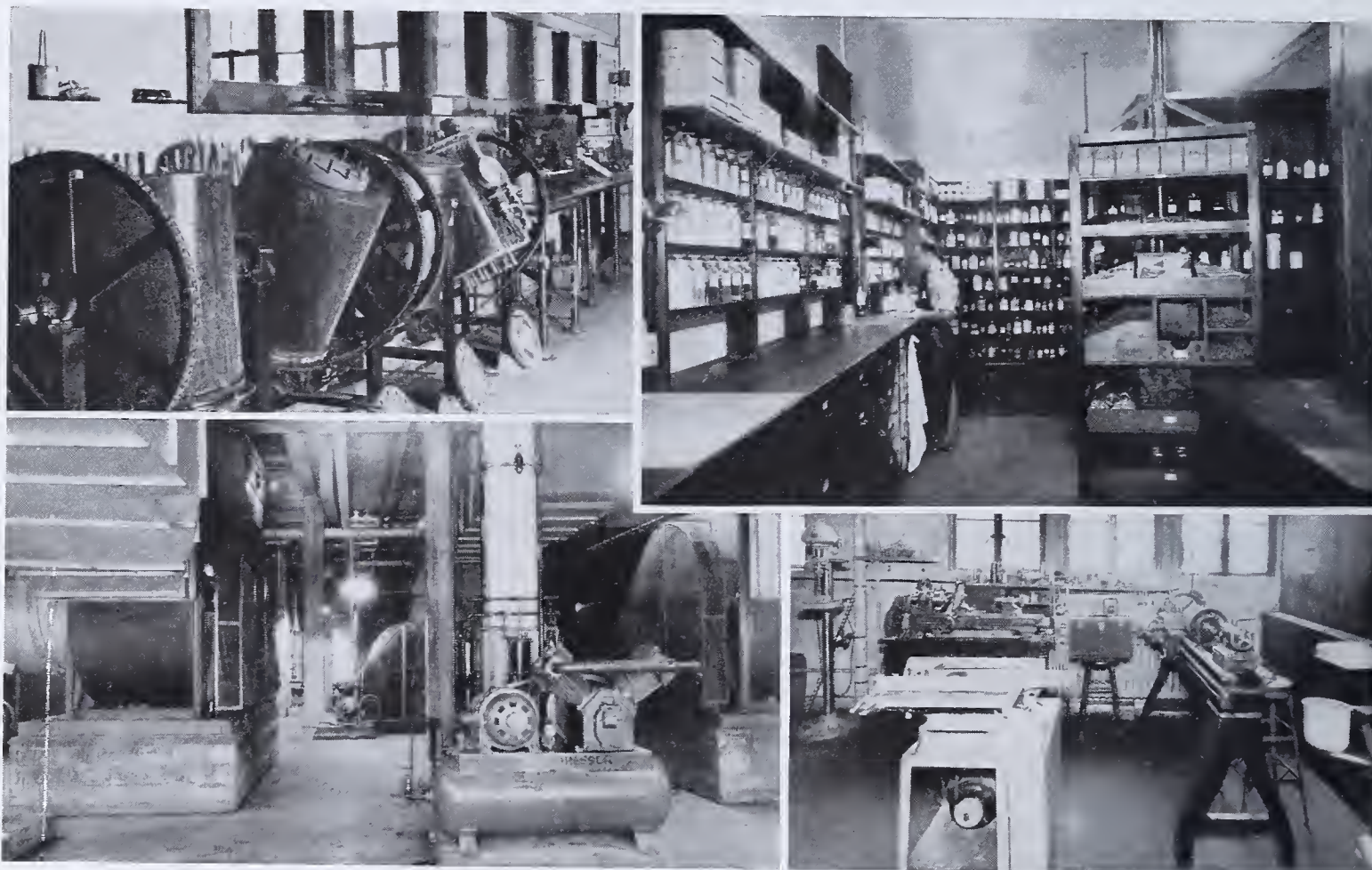
The laboratory for unit operations has space for such tall equipment as absorption towers, fractionating columns, and

#### LABORATORY SPACE DISTRIBUTION

	Maximum Student Capacity	Total Floor Area Sq. Ft.
Ground or First Floor		
Physical chemistry	144	2050
Advanced physical chemistry	12	700
Electrochemistry	45	770
Industrial chemistry	84	1650
Unit processes	72 <sup>a</sup>	1800
Unit operations	80 <sup>a</sup>	5400
Chemical engineering undergraduate research	63	880
Graduate research	56	4655
Total	556	
Main or Second Floor		
Biochemistry	108	1030
Advanced biochemistry	10	450
Microchemistry	30	590
Quantitative chemistry	240	3600
Advanced quantitative chemistry	36	1000
Library	48	1800
Graduate research	24	3000
Total	496	
Third Floor		
Inorganic and general chemistry	2563	8000
Advanced inorganic chemistry	10	520
Organic chemistry	429	4450
Advanced organic chemistry	10	750
Graduate research	25	2500
Total	3037	

<sup>a</sup> Based on six hours per week per student.





*Upper left.* BATTERY OF DIGESTERS IN WOOD PULP LABORATORY. *Upper right.* ONE OF FOUR ROOMS IN DISPENSING SERVICE. *Lower left.* VENTILATION AND MECHANICAL ROOM. *Lower right.* CORNER OF MACHINE SHOP

evaporators. Equipment for the study of crushing, grinding, and separation of solids is located in a small adjacent room for the localization of any dust problems. Other noteworthy features are positive floor drainage, equipment anchors along the walls, chimney flue through the roof, an ice machine for supplying refrigeration to equipment, and a 5-ton overhead traveling crane. The floors or ceilings over this laboratory have been fitted with cored holes each of approximately 1 square foot area, so that apparatus requiring 60 feet of elevation may be installed.

The importance of the pulp and paper industry in the Pacific Northwest and the need for adequate training of graduates entering that field led to the inclusion of a series of laboratories specially equipped for class work and research in this field. A small digester room contains a waste gutter, a special chimney flue with individual fan to remove relief gases, four rotating digesters for sulfite and alkaline cooking, a semiplant stainless-steel digester with external heating and circulation; also necessary washers, screens, beater, bleacher, thickener, and test equipment for the pulp produced.

Situated between the pulp laboratory and the unit process laboratory is the control laboratory where chemical control tests are performed in the semiplant processes in chemical industry; the student may operate these on a small scale.

A number of special laboratories are provided. A large laboratory for research in unit operations and high-pressure reactions adjoins the unit operations laboratory and has large service lines, floor gutter, keyhole equipment, anchor standards, and other features. A high-pressure compressor furnishes compressed gases for hydrogenation and studies in high-pressure operations. A large-capacity blower furnishes air for submerged combustion investigations. Another laboratory contains space for sixty undergraduate students for

senior thesis work. The control laboratory is designed for use by students doing research on pulp and paper, or unit process problems. Many small laboratories for individual students are available for carrying on advanced problems.

THE mechanical equipment of the building is necessarily extensive and intricate. Dictates of economy and maintenance resulted in exposed piping on ceilings with most vertical work concealed in shafts. Ventilation of the entire building is by means of warmed washed air from basement fans and foul air is removed by exhaust fans in roof level rooms. Although no cooling coils have been installed, the temperature of the water used in washing the air and the general climate of the region assure a definite lower differential within the laboratories on the hottest summer days.

The following are required for the operation of the building:

Plenum fresh air, cubic feet per minute	18,500
Total air supply, cubic feet per hour	9,000,000
Hood exhaust fans	46
Transformer room, cubic feet	10,000
Lighting intensity: 15 foot-candles over all laboratory tables and 20 foot-candles in lecture rooms.	

Fume exhaust system: vitrified tile pipe.

Waste lines: extra heavy cast iron with ceramic tile for vertical risers in concealed work.

Steam is obtained at boiler pressure from the central plant of the university at 185 pounds and distributed in the building at 125, 15, and 2 pounds.

Black enamel cast-iron sinks are used throughout. These are fitted with Corrosiron plugs and tailpieces to the waste lines. Laboratory benches were designed by the separate divisions and constructed locally. Birch tops of 2-inch stock and fir frames were selected. Gutters were entirely eliminated, each student having access to a sink. The student capacity of the General Chemistry Laboratories was increased 300 per cent by replacing the drawer and locker type of desk by that of the single drawer.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Total Dissolved Solids in Water by Electrical Conductivity

H. GUSTAFSON AND A. S. BEHRMAN, International Filter Co., Chicago, Ill.

THE determination of total dissolved solids in natural waters may at times serve a number of different purposes, but the principal value of the measurement in a fairly complete mineral water analysis is to check the sum of the constituents as individually determined or calculated. Lack of reasonably good agreement between the total solids determined as such and the total solids as calculated from the analytical data is usually evidence either of an error in analysis or computation, or of the presence in important quantity of some substance that has been overlooked in the analysis.

For example, the usual practice in water analysis does not determine the alkali metals directly, but calculates and reports in terms of sodium the stoichiometric alkali metal equivalent of the excess of anions remaining after combination or comparison with the determined calcium and magnesium. Since nitrates are not usually determined in the ordinary mineral water analysis, it would thus be possible to overlook completely a large quantity of sodium nitrate unless some method is provided for bringing the omission to light. The determination of total dissolved solids accomplishes this purpose.

If it is to serve its purpose well, the total solids determination must be dependable when applied to all types and concentrations of waters and must have an accuracy comparable with that of other analytical methods employed. For practical reasons, the procedure should require a minimum of time and labor.

The usual method of determining total solids by evaporating a measured volume of water and drying the residue at a definite temperature is not entirely satisfactory. Complete dehydration of the residue can-

not be secured in all cases without serious loss of certain mineral constituents, particularly chlorides and nitrates (1). The presence of organic matter and fine suspended material often adds to the difficulty of the determination.

As an alternative to the measurement of total solids by weight, electrical conductance has been employed for a number of years in certain special applications, as in detection of condenser leakage, examination of boiler and irrigation waters (2, 4, 5), and as a rapid means for following fluctuations in a particular water. The conductivity method has consistently been described as approximate; several investigators have shown that a simple factor cannot be applied for all types of

waters or for different concentrations of the same type of water. Recently, however, Kitto (3) has described a conductivity procedure wherein electrical conductance and analytical data are employed in the estimation of total solids; while the method appears rather complicated and cumbersome, it does constitute a direct effort to take into consideration the nature of the chemical compounds present when interpreting conductance measurements.

The method of determining total solids by conductance devised by the present authors is based on a recognition of the quantitative influence of the nature of the compound on the conductance. One of the first steps in devising the method, therefore, was a series of measurements of conductance values for the various electrolytes commonly found in natural waters, and for the low concentrations normally encountered. These concentrations range in general from a few to several thousand parts per million (roughly 0.0001 *N* to 0.1 *N*). In order to avoid complicating

The principal utility of the determination of total solids in a reasonably complete mineral analysis of water is to provide a check on the other analytical data. The standard method of determining total solids is to evaporate a measured volume of the water and dry the residue at a specified temperature to constant weight. This usually requires several hours and an appreciable amount of labor; furthermore, the procedure is not always a satisfactory one, since its accuracy must depend on heating the residue to a temperature high enough to ensure complete dehydration without causing any chemical decomposition.

Electrical conductance has been utilized for many years as a rough empirical index of the total solids content of a water, and has been put to practical use in such applications as the detection of condenser leakage. Efforts to use conductance as a quantitatively accurate measure of total solids, however, have generally been unsuccessful, because of the materially different conductance values of the various compounds present in nearly all waters.

The present authors have determined the conductance values in dilute solutions of the compounds involved, and have devised a method whereby a single, quickly made conductivity measurement serves as an accurate check of the total solids calculated from the chemical analysis. Consistent accuracy has been observed in using the method in the analysis of well over a thousand water samples; and the determination is now employed in place of the evaporation method as a routine procedure.



TABLE I. SPECIFIC CONDUCTIVITY OF 0.001 N SOLUTIONS				
Salt	Concentration Normality	P. p. m. as CaCO <sub>3</sub>	Specific Conductivity at 25° C. (× 10 <sup>5</sup> )	
			Determined	Calculated
Mg(HCO <sub>3</sub> ) <sub>2</sub>	0.00127	63.5	11.55	
MgSO <sub>4</sub>	0.00127	63.5	14.7	14.4
MgCl <sub>2</sub>	0.00127	63.5	15.4	15.35
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.00127	63.5	14.95	14.7
Ca(HCO <sub>3</sub> ) <sub>2</sub>	0.001005	50.3	9.77	
CaSO <sub>4</sub>	0.001005	50.3	12.2	12.0
CaCl <sub>2</sub>	0.001005	50.3	12.8	12.8
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.001005	50.3	12.75	12.3
NaHCO <sub>3</sub>	0.00099	49.5	9.08	
Na <sub>2</sub> SO <sub>4</sub>	0.00099	49.5	12.3	12.1
NaCl	0.00099	49.5	12.3	12.3
NaNO <sub>3</sub>	0.00099	49.5	11.7	11.8

TABLE II. CONDUCTIVITY PER PART PER MILLION			
Salt	Normality	Specific Conductivity per P. p. m. at 25° C. (× 10 <sup>5</sup> )	
			Av.
Mg(HCO <sub>3</sub> ) <sub>2</sub>	0.00127	0.182	
Ca(HCO <sub>3</sub> ) <sub>2</sub>	0.001005	0.194	0.186
NaHCO <sub>3</sub>	0.00099	0.183	
MgSO <sub>4</sub>	0.00127	0.231	
CaSO <sub>4</sub>	0.001005	0.242	0.240
Na <sub>2</sub> SO <sub>4</sub>	0.00099	0.248	
MgCl <sub>2</sub>	0.00127	0.243	
CaCl <sub>2</sub>	0.001005	0.254	0.249
NaCl	0.00099	0.249	
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.00127	0.235	
Ca(NO <sub>3</sub> ) <sub>2</sub>	0.001005	0.253	0.241
NaNO <sub>3</sub>	0.00099	0.236	

TABLE III. SPECIFIC CONDUCTIVITY OF SYNTHETIC WATERS								
Water	Composition						Conductivity at 25° C. (× 10 <sup>5</sup> )	
	Ca	Mg	Na	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	
	Parts per Million as Calcium Carbonate							Determined    Calculated
1	25.1	0	24.7	25.1	24.7	0	0	10.7    10.6
2	0	31.7	24.7	24.7	31.7	0	0	12.0    12.2
3	0	31.7	24.7	31.7	24.7	0	0	11.8    11.8
4	25.1	31.7	0	31.7	25.1	0	0	11.9    11.9
5	12.6	12.7	27.2	18.9	21.2	12.4	0	11.8    11.7
6	5.0	0	44.5	29.7	14.8	5.0	0	10.7    10.3
7	17.6	9.5	24.8	2.5	34.5	9.9	5.0	12.4    12.4
8	27.7	12.7	12.4	10.1	5.0	37.7	0	12.7    12.5
9	3.5	1.9	44.6	45.0	2.5	2.5	0	9.8    9.6
10	35.3	12.7	5.0	48.0	2.5	2.5	0	10.4    10.2

factors existing in the more concentrated solutions, it appeared desirable to determine conductivities at a concentration as low as practicable. To eliminate the necessity for correction for the diluting medium (ordinary distilled water aerated to remove free carbon dioxide), the dilution must be limited to such a point that the conductance of the diluting medium is unimportant compared with the conductance of the solution. The specific conductance of the aerated distilled water used by the authors is about  $2 \times 10^{-6}$  reciprocal ohm which is about 1.5 per cent of the conductance at 0.001 *N*, the concentration selected by the authors for the modification of the method finally adopted, and which is reported here.

The ratio  $\frac{\Lambda}{\Lambda_0}$  for 0.001 *N* solutions is about 0.98 for uni-univalent electrolytes—e. g., sodium chloride—0.94 for uni-bivalent electrolytes—e. g., sodium sulfate—and 0.86 for bi-bivalent electrolytes—e. g., calcium sulfate. Specific conductivities calculated from published values for  $\Lambda_0$  using the above-mentioned conductance ratios are compared in Table I with values obtained by the authors at concentrations of approximately 0.001 *N*.

Preparation of Standard Solutions

Solutions of sodium bicarbonate (from c. p. NaHCO<sub>3</sub>), calcium bicarbonate (by carbonating a slurry of c. p. CaCO<sub>3</sub>), and of magnesium bicarbonate (by carbonating c. p. MgCO<sub>3</sub>) were prepared in concentrations ranging from about 0.02 to 0.1 *N*.

To prepare the approximately 0.001 *N* solutions required, the proper volumes of the strong solutions were transferred by pipets to 1-liter volumetric flasks, diluted with distilled water, aerated to remove free carbon dioxide, and finally diluted to the mark with aerated water at a temperature of 25° C. Sulfate, chloride, and nitrate solutions of the same equivalent strengths were made by placing the same quantities of the strong bicarbonate solutions in 1-liter flasks, adding the proper volume of 0.1 *N* acid solution, aerating to remove carbon dioxide, and diluting to the mark with aerated distilled water at 25° C. A dip-type conductivity cell with cell constant 0.0963 was used. (Cell constant was determined with a 0.001 *N* solution of sodium chloride.)

From the determined values given in Table I were calculated the conductivities per part per million at the concentration stated (Table II).

Conductivity Determination of Total Solids

It seemed possible that the data of Tables I and II might serve as a basis for calculating the conductivity of 0.001 *N* solutions of known composition. Comparison of this calculated value with the measured conductivity, also at 0.001 normality, would serve to check the sum of the total solids computed from the other analytical data. With this thought in mind, various waters of accurately known composition and approximately 0.001 *N* were prepared and conductivities measured. Table III shows the analysis of these waters, the

determined specific conductivity, and the calculated conductivity. Calculated conductivity equals the sum of HCO<sub>3</sub> × 0.186, SO<sub>4</sub> × 0.240, Cl × 0.249, and NO<sub>3</sub> × 0.241. Most of the synthetic waters listed in Table III are similar in composition to natural waters. It will be noted that the maximum deviation of the calculated from the observed values is 4 per cent. In all cases, agreement is sufficiently good for the intended application of the procedure.

For applying the method to natural waters, several somewhat different procedures were tested. The one finally adopted, and now employed as a routine procedure in the

TABLE IV. DILUTION TABLE			
Total Solids from Analytical Data P. p. m. as CaCO <sub>3</sub>	To Dilute to 250 Cc.	Dilution Factors, Multiply by:	
	Cc.		
0 to 55	250		1.00
55 to 75	200		1.25
75 to 100	140		1.79
100 to 150	100		2.50
150 to 200	70		3.57
200 to 300	50		5.00
300 to 400	35		7.15
400 to 560	25		10.0
560 to 700	20		12.5
700 to 1000	15		16.7
1000 to 1500	10		25.0
1500 to 2000	7		35.7
2000 to 3000	5		50.0



TABLE V. CONDUCTIVITY OF NATURAL WATERS

Water	Composition							Conductivity at 25° C. (× 10 <sup>5</sup> )	
	Ca	Mg	Na	HCO <sub>3</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	Determined	Calculated
	Parts per Million as Calcium Carbonate								
1	375	200	18	270	313	10	0	130	128
2	160	120	939	172	17	1030	0	298	293
3	8	7	28	2	31	10	0	8.8	10.3
4	282	66	166	210	157	147	0	116	113
5	97	42	32	80	83	8	0	37.6	36.8
6	2	6	485	334	104	55	0	104	101
7	5	4	17	5	1	4	16	5.3	6.0
8	16	6	9	17	10	4	0	6.5	6.5
9	205	18	24	169	31	23	24	53.3	50.3
10	270	82	831	350	3	830	0	280	272
11	12	20	827	396	349	114	0	183	186
12	92	112	449	76	259	318	0	154	155
13	687	400	117	244	954	6	0	278	276
14	32	26	9	53	10	4	0	13.4	13.2

TABLE VI. DETERMINATION OF NONCARBONATE SOLIDS

Water	Carbonate Solids	Noncarbonate Solids	
		Conductivity method	By analysis
		P. p. m. as CaCO <sub>3</sub>	
1	270	320	323
2	172	1064	1047
3	2	34	41
4	210	308	304
5	80	91	91
6	334	168	159
7	5	17	21
8	17	13	14
9	169	88	78
10	350	860	833
11	396	438	463
12	76	560	577
13	244	930	960
14	53	14	14

laboratories of the writers' organization is essentially as follows:

The water sample is diluted in accordance with the amount of dissolved total solids (exclusive of silica) computed from the chemical analysis to provide a concentration of 40 to 60 p. p. m. as calcium carbonate. (Table IV was prepared to facilitate the diluting procedure.) Air is then bubbled through the diluted sample to remove free carbon dioxide. If necessary, the temperature is adjusted to 25° ± 3° C. The conductivity is now determined in any suitable manner. The authors employ the familiar combination of (1) the slide wire of a Leeds & Northrup potentiometer, (2) a resistance box, (3) a microphone hummer as a source of high-frequency current, and (4) a dip-type conductivity cell. The measured conductivity is corrected to 25° C. by use of the usual correction of 2 per cent per degree rise in temperature.

The natural waters listed in Table V show the agreement obtained with highly different types of mineralization. Determined conductivity equals conductivity at 40 to 60 p. p. m. concentration multiplied by the dilution factor. Calculated conductivity equals the sum of the values obtained by multiplying the bicarbonate, the sulfate, the chloride, and the nitrate (all as calcium carbonate) by 0.186, 0.240, 0.249, and 0.241, respectively. Inspection of a large group of samples indicates that the agreement between determined and calculated conductivities in Table V is perhaps a little poorer than average. The per cent difference between total solids computed from the analysis and total solids by conductivity is readily obtainable by comparison of corresponding calculated and determined conductance values. Actual total solids by conductivity are secured by multiplying the sum of either the cations or the anions by the ratio of determined to calculated conductivity.

Examination of the data in Table V will show that the per cent differences between determined and calculated values are less than 4 per cent (the maximum difference in Table IV) in 11 of the 14 samples. Deviations exceed 4 per cent in samples 3, 7, and 9. In terms of parts per million, the differences amount to 6, 3, and 15 parts per million,

respectively. Consistent accuracy of the same order has been observed in the analyses of well over a thousand samples of water in which the conductometric determination of total dissolved solids has been employed instead of the evaporation method.

Rapid Determination of Noncarbonate Solids

The conductometric procedure for total solids presents an opportunity for a rapid, partial water analysis of considerable usefulness in connection with two rather recent developments in water treatment: hydrogen zeolite and anion exchangers. The two determinations, alkalinity and conductivity, when used in the formula below give carbonate and noncarbonate solids, the essential values for engineering calculations pertaining to hydrogen zeolite or to hydrogen zeolite followed by anion removal. The sample should be diluted to a specific conductivity lying between 9 × 10<sup>-5</sup> and 13 × 10<sup>-5</sup> reciprocal ohm. The value obtained is then multiplied by the dilution factor.

Conductivity (× 10<sup>5</sup>) - (alkalinity × 0.186)

0.25

= noncarbonate solids as calcium carbonate

The determinations and calculation require only a few minutes and results are amply accurate for the purpose served. The usual procedure, involving analysis for sulfate, chloride, and nitrate as well as alkalinity, requires several hours' time. Calculations have been made from the data of Table V to illustrate the usefulness of this simple procedure (Table VI).

Summary

Determination of conductivity as described serves as a reliable rapid means of verifying the sum of the total solids computed from the other analytical data. The procedure is applicable to all different types of waters ordinarily encountered and accuracy is consistent over the entire range of concentration of natural waters. In addition, the conductivity procedure provides means for a rapid estimation of noncarbonate solids, a determination ordinarily obtainable only at the expenditure of considerable time and effort.

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# The Rigidity of Starch Pastes

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MAXWELL (13) in 1868 proposed an equation relating the rigidity of a body to its viscosity by means of the relaxation time. Twenty years later, Schwedoff (21) devised an apparatus for measuring the rigidity and relaxation time of sols. He stated that the viscosity of a liquid is not necessarily an index of its rigidity. A number of investigators (6, 17, 22) have since worked out formulations for structural viscosity on the assumption that it is due to the presence of elasticity. [Rigidity is the reciprocal of elasticity. For definitions, see (3).]

Michaud (14, 15), by an ingenious method of his own, investigated the effect of acids, bases, salts, and some organic compounds on the rigidity of gelatin and agar gels. Philip-poff (18) described a dynamic method for determining elasticity of cellulose solutions, while Neale (16) measured the elasticity of air-dried starch films.

Porst and Moskowitz (19) summarized Bingham's concept of rigidity as applied to starch. Their attempts to measure the "yield shear value" by extrapolation of flow-shear curves gave indefinite results because of the gradual slope of the curves obtained. Farrow, Lowe, and Neale (7), using both capillary and Couette-type viscometers, observed flow in starch pastes at rates of shear below Bingham's theoretical "yield value."

McDowell and Usher (12) advanced a simple mechanical explanation, supported by striking experimental evidence, for the phenomena of rigidity and anomalous viscosity in suspensions and gels: "If rigid particles suspended in a liquid in which they are insoluble are not prevented from cohering—whether by an electric charge or by an envelope of a soluble substance—they will in time form aggregates, the presence of which will always cause the viscosity to be a function of the rate of shear; and which, if completely interlinked, will impart rigidity to the suspension as a whole." They mention that variable viscosity is shown sometimes when rigidity is absent, and always when it is present.

Hess and Rabinowitsch (9), after heating starch grains just above their gelatinization temperature, punctured the granule membrane with a microneedle and photographed a liquid oozing out at the point of puncture. They believe that swollen starch grains have a certain amount of inner structure which, like the membrane, possesses elasticity. Badenhuizen (2) described experimental evidence which would seem to contradict this concept of granule structure.

Woodruff and MacMasters (23) made measurements of relative viscosity and gel strength on starches from different varieties of corn and on starches from the same variety of corn treated in different ways. They found that viscosity differences were very small as compared with differences in gel strength and that the two properties frequently did not fluctuate in the same direction. They give this as further evidence that viscosity and gel strength seem to measure two different sets of properties in the starch.

Most of the methods now in use for the determination of gel strength in starch pastes involve actual disruption of their structure—i. e., measure the degree to which they can be stretched before breaking. This value fluctuates with the rate at which the force is applied, so that a high degree of accuracy is not obtained.

The method developed by Schwedoff (21) measures the resistance offered by the paste to being stretched. The results are more accurate, since the gel is not deformed beyond its

elastic limit, and the values obtained are independent of apparatus constants. By this means, rigidity has been demonstrated in a variety of gels (1, 8, 10, 11, 15, 18, 20, 21), but in only two cases has mention been made of starch: McDowell and Usher (11) measured the rigidity of non-aqueous suspensions of raw starch, and Arcay and Etienne (1) included starch in the list of substances whose gels they tested for the presence of rigidity.

Caesar (4, 5) has designed a consistometer for characterizing starch pastes by their relative resistance to violent mechanical agitation at high concentrations (10 to 30 per cent). Consistency, as measured by this method, is partly conditioned by rigidity, as well as by viscosity, plasticity, and thixotropy.

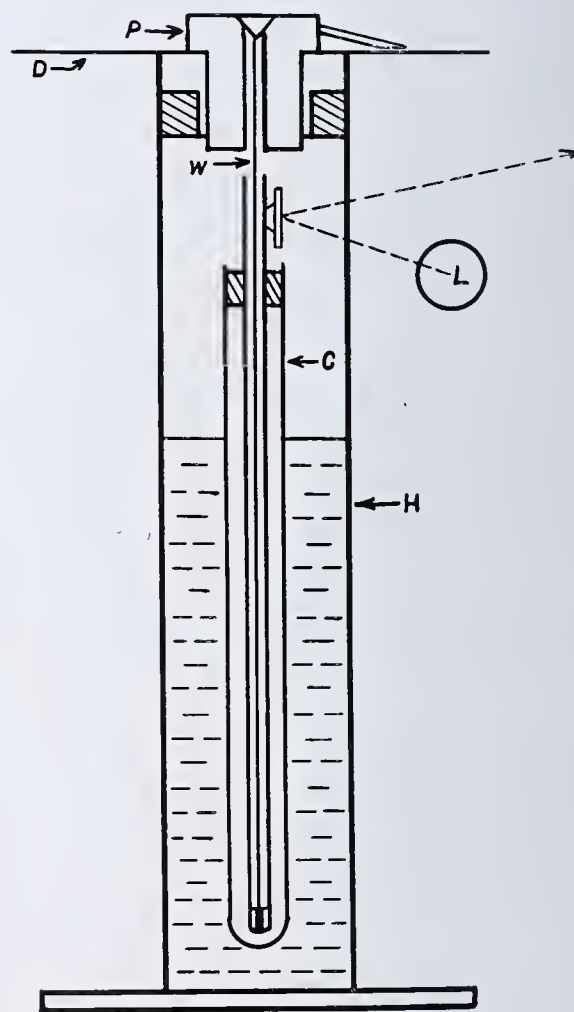


FIGURE 1. DESIGN OF RIGIDOMETER

The results obtained from the application to starch pastes of the Schwedoff technique for measuring rigidity are reported in this paper.

## Experimental

DEMONSTRATION OF RIGIDITY IN STARCH PASTES. Preliminary experiments were made using a MacMichael viscometer. The paste, after cooling, was placed in the viscometer cup and a definite twist given to the wire. With pastes of low concentration, the disk eventually swung back to its original position, but if the concentration was high



enough, it came to rest before reaching the zero point, thus demonstrating the presence of elasticity.

However, any disturbance of the paste—even the passage of the disk attached to the wire during measurements—resulted in a breaking up of the gel structure and subsequent lowering of elasticity values. Since this factor made it difficult to obtain accurate and reproducible results, the design of the MacMichael viscometer was modified into an apparatus resembling Schwedoff's (21) for the quantitative determination of rigidity.

**DESCRIPTION OF RIGIDOMETER.** The design is illustrated in Figure 1. A MacMichael viscometer wire, *W*, encased in a metal shaft, hangs from the bottom of a dial, *D*, graduated in degrees. By means of a piece of rubber tubing, the shaft around the wire is firmly attached to a small glass cylinder, *C*, so that the latter may hang freely inside a larger cylinder, *H*. A mirror on the shaft reflects a beam of light from its source, *L*, onto a graduated scale in front of the apparatus.

If water or other ideal liquid is placed in the larger cylinder, the angle through which the wire is turned by the dial will be identical with the angle through which the cylinder turns in the liquid (as read by the position of the light beam on the scale). If a paste showing rigidity is placed in the larger cylinder, the inner cylinder will be deflected (when a torque is applied to the wire) by an amount depending on the elasticity of the paste, providing the force applied through the wire is not great enough to cause shear of the paste structure.

Two modifications of this apparatus have been used. For most of the experimental work reported in this paper, the outer glass cylinder, *H*, and the calibrated dial, *D*, were mounted independently in a rigid brass frame inside a constant-temperature air bath. When the inner cylinder had been set in place and secured by means of screws through a brass collar, the paste was poured in through a hole in the side of the outer tube and the inner cylinder released by turning back the screws. A mirror was also attached to the dial to provide for extra precision in setting and reading.

The second modification which is shown in Figure 1 was developed later to allow for greater convenience and speed of handling. Hydrometer cylinders (250-cc. capacity) were used for the outer tubes. The paste was poured in through the top, the calibrated dial put in place, and a center piece, *P*, bearing the wire and inner cylinder lowered into it. The whole unit was then set in a constant-temperature water bath until equilibrium was reached and finally moved over to the light source for measuring.

The first method is the more precise, while the second method is simpler in operation. In the first-described apparatus, the paste may be poured in after it has been cooled and requires only about 3 hours to reach equilibrium. The unit is not moved from the time the paste is put into it.

In the second modification, the paste must be poured in while hot, so that it will be fluid enough for the inner cylinder

to center itself. A paste prepared in this manner and placed in a 25° C. water bath requires at least 10 hours to reach equilibrium. No skin is formed on the surface of the paste, however, since the top piece prevents appreciable evaporation.

**STANDARDIZATION OF PROCEDURE.** Experiments were first carried out to determine the effect of time and temperature on rigidity. If, as McDowell and Usher (12) imply, anomalous viscosity is correlated with rigidity, then a 5 per cent cornstarch paste which shows abnormal viscosity at 90° C. should also show rigidity at that temperature. Such was found to be the case. The rigidity increases with time of standing in an irregular manner during the first 3 hours at 90°. Measurements taken after 3 hours at this temperature are subject to error because of evaporation of water from the paste. In order to eliminate this difficulty, the pastes were first heated to 90° and then cooled to 25° before being allowed to set. The resulting data showed that rigidity increases rather rapidly with time during the first 3 hours and then becomes nearly constant. (This holds for the unmodified starches under the conditions of experiments reported. It is likely that the time required varies with the concentration and previous treatment of the starch.) Lampitt and Money (10) have obtained similar results with pectin gels.

During measurements of elasticity, it is possible, by imparting sufficient twist to the wire, to strain the paste beyond its elastic limit and shear it. At this point the gel ruptures and the inner cylinder drifts along in the direction of twist on the wire. With pastes of fairly low elasticity this point is evident as a well-defined break, but with pastes of high elasticity it cannot be accurately detected. Tendency to shear, expressed in reciprocal form as shear value, must be considered because of its important effect on rigidity values. (Shear value is the torsional moment of the wire, *N*, multiplied by the number of degrees through which the wire may be twisted before shearing the paste.) Shearing tends to break up gel structure, so that once a paste has been sheared it is useless to make further rigidity measurements on it. If a certain paste shears so easily that its rigidity is difficult to determine, the shear value may be increased by using a higher concentration of paste, or by preparing the paste at a higher temperature, providing the granules have not been ruptured. The use of a lighter wire (one having a lower torsional moment) facilitates the measurement of pastes with low shear values.

**PROCEDURE.** The studies on the effect of time, temperature, and shear led to the adoption of the following method for determinations of rigidity:

The weighed starch sample, suspended in 200 cc. of distilled water, is heated at the desired temperature in a water bath until it has come to equilibrium. This requires approximately 60 minutes of heating at 70° C., 50 minutes at 80°, 40 minutes at 90°, and 30 minutes at 99°, as determined by the change in volume of centrifuged granules at regular time intervals. The paste is then cooled to 25° by shaking in a stream of running water and poured into the tubes of the rigidometer where, after standing undisturbed for 3 hours, it is measured by placing varying degrees of twist,  $\delta$ , on the wire and noting the corresponding deflection,  $\omega$ , of the cylinder. These two values,  $\delta$  and  $\omega$  (converted to angular degrees), when plotted against one another, make a straight line. Then the slope of this line,  $\delta/\omega$ , may be substituted in the equation mentioned by Hatschek and Jane (8):

$$E = \frac{N}{4\pi h} \left( \frac{1}{R_0^2} - \frac{1}{R_1^2} \right) \frac{\delta}{\omega}$$

where *E* is the modulus of rigidity in dynes per square centimeter; *N*, the torsional moment of the wire used; *h*, the height of the paste on the inner cylinder; and *R*<sub>0</sub> and *R*<sub>1</sub>, the radii of the

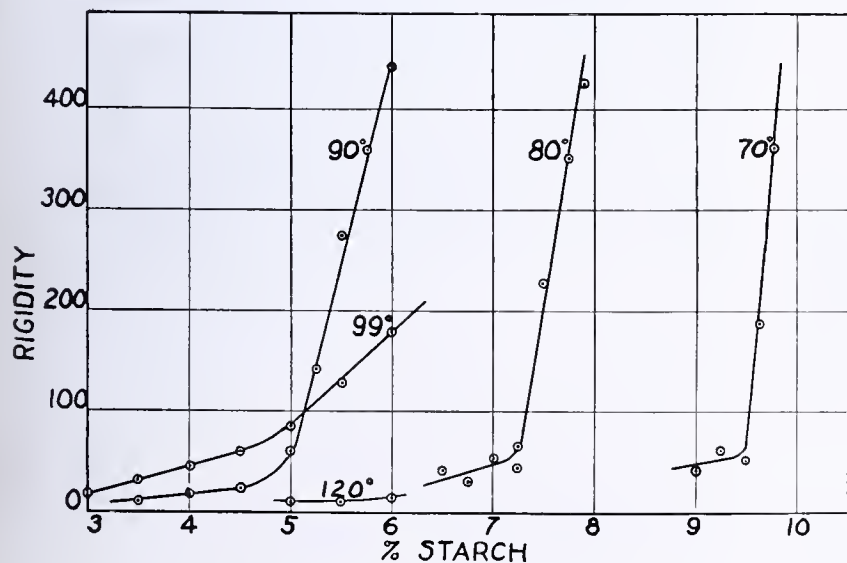


FIGURE 2. RIGIDITY-CONCENTRATION CURVES FOR CORNSTARCH PASTES PREPARED AT DIFFERENT TEMPERATURES



inner and outer cylinders, respectively. (The wires were standardized by measuring the oscillation time of a suspended disk of known mass. Then  $N = 4\pi^2 MR^2/2T^2$ , where  $T$  is the period of oscillation and  $M$  and  $R$  are the mass and radius of the disk used.) Wires with torsional moments of 0.0256, 0.0665, and 0.1460 erg were used interchangeably with entirely consistent results, showing that wire size may be suited to the strength of the paste being measured without introducing error in this respect.

### Characterization of Starches by Means of Rigidity

A comparison was made of three different starches showing extreme variation in physical properties: a commercial cornstarch, tapioca starch, and waxy maize starch, which gives a reddish brown color with iodine.

Figure 2 shows rigidity-concentration curves for the commercial cornstarch. At 70°, 80°, and 90° C. the curves are nearly identical in shape, the rigidity changing very slowly up to a certain critical concentration, above which it increases enormously for each slight increase in the percentage of starch. If the lower arm of the curve at 90° is extrapolated, it intersects the X-axis at approximately the same concentration at which structural viscosity sets in, 2.7 per cent. The same thing appears to be true of the curves at 70° and 80°, although they cannot be accurately extrapolated because the high tendency to shear makes rigidity values uncertain at lower concentrations. Above 90° a change in the condition of the granules begins to set in, and at 99°, instead of bending sharply and shooting upward almost vertically, the curve slopes upward only gradually. Finally, a paste heated in the autoclave at 120° shows comparatively little rigidity.

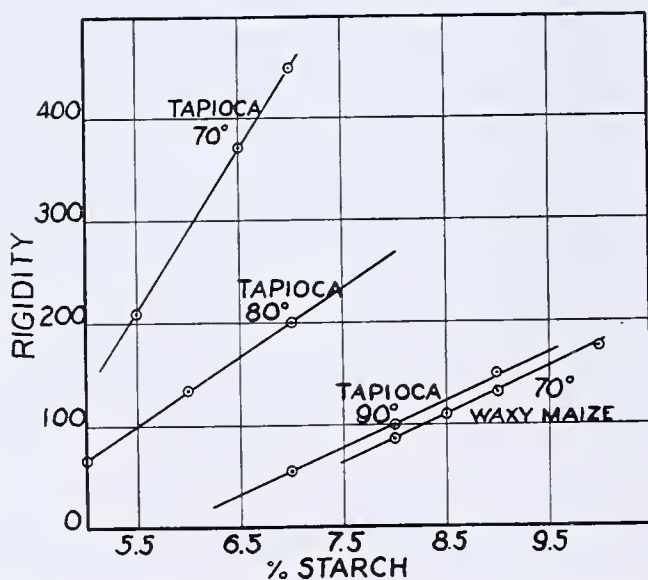


FIGURE 3. RIGIDITY-CONCENTRATION CURVES FOR TAPIOCA AND WAXY MAIZE STARCH PASTES PREPARED AT DIFFERENT TEMPERATURES

With tapioca (Figure 3), it is evident that even at 70° changes have begun to take place in this starch, and the slope of the rigidity-concentration curve decreases progressively with increasing temperature of preparation. Rigidity in waxy maize, even at 70°, is very low and at 75° is no longer evident. Rigidity increases in strictly linear relationship to concentration after the initial bend in the curve has been passed, the bend being more or less sharp depending upon the degree to which the paste has been altered at that temperature.

Another method of treating these data is illustrated in Figure 4, where rigidities at a given concentration of paste are plotted against temperature. This type of curve shows the temperature at which each starch exhibits its maximum rigidity. Tapioca and commercial cornstarch give curves

very similar in shape, differing only in the temperature required to produce rigidity. Waxy maize has nearly the same temperature of maximum rigidity as tapioca, although a much higher concentration of the former is needed to produce the same amount of rigidity.

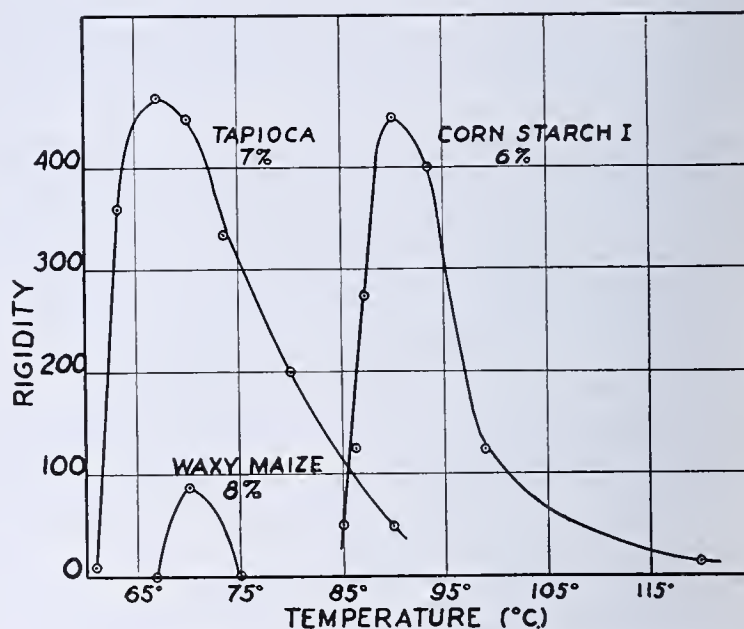


FIGURE 4. EFFECT OF TEMPERATURE OF PREPARATION ON RIGIDITY OF THREE STARCHES

It is interesting to compare these curves with the consistency-temperature curves obtained by Caesar (4, 5). Although very similar in shape, they are quite different quantitatively because of the difference in properties measured and methods employed.

### Differentiation of Cornstarches

Having tried out rigidity measurements on different kinds of starch, an attempt was next made to apply them to different varieties of the same starch. Rigidity-concentration curves (Figure 5) were obtained on seven different cornstarches prepared in the small-scale milling plant in this laboratory and on two commercial cornstarches. In all cases the pastes were made up at 99° C. and measured at 25°.

Samples of these starches in 2.7 per cent concentration were then prepared at 99°, cooled to 25°, and viscosities determined by the capillary method. Table I is characteristic of the results obtained.

Since viscosity in pastes of this concentration varies with pressure, the viscosity values are given at three different pressures: at 5 cm. of water, where the decrease in viscosity with increasing pressure is extremely rapid; at 15 cm., where the bend in the viscosity-pressure curve is most pronounced; and at 30 cm., where the curve has leveled off and viscosity remains practically constant with further increase in pressure. The lack of correlation between rigidity and viscosity values indicates that they measure different properties of the pastes.

### Relation of Granule Membrane to Rigidity

The downward trend of the rigidity-temperature curves after reaching their maximum (Figure 4) has been ascribed above to a change in the condition of the granules. In order to get a better insight as to the character of this change, microscopic technique was employed. A glass cell mounted in a hot-plate substage provided the means for observing the progressive swelling of granules in water suspension inside the cell. It was noted with tapioca and waxy maize starch that after the temperature of maximum rigidity had been reached,



the granules, rather than increasing further in size, began to become more wrinkled, the degree of wrinkling increasing with temperature. At the same time, the refractive index of the granules approached so nearly that of water that it was difficult to observe them. It appeared as though the membrane became so permeable that it offered no resistance to the free exchange of contents with the outside medium. In general, no distinct rupture or breaking open of the granule membrane could be observed.

Since the cornstarch grains failed to exhibit any notable change under the microscope at the temperature of maximum rigidity, they were modified by various methods designed to weaken the membrane. Table II shows that when the granule membrane is weakened, whether by heat, mechanical treatment, or chemical degradation, rigidity decreases.

Discussion

Although not often encountered in the literature, the lack of correlation between viscosity and gel strength of starch pastes is generally recognized in the industry.

The relationship between breaking strength and elasticity is less definite. Rigidity measurements are made without shearing the pastes, presumably giving a method of characterizing the starch independent of its viscosity and plasticity. It might be said that the rigidity and breaking strength of a starch are related as are the elasticity of a steel beam and the force required to break it. In preliminary experiments there were found cases where these two properties differed decidedly, but more often they paralleled one another.

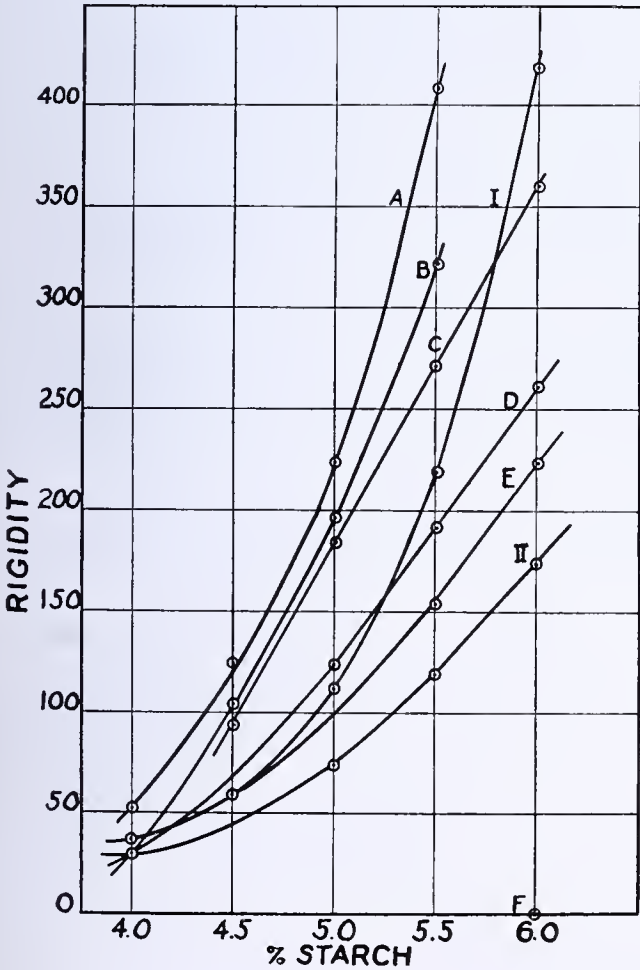


FIGURE 5. RIGIDITY-CONCENTRATION CURVES FOR CORNSTARCH PASTES PREPARED AT 99° C.

- A. Popcorn
- B. Yellow Creole and Iowa
- C. Iogent
- D. Reid Yellow Dent
- E. Country Gentleman
- F. Waxy maize
- I, II. Commercial starches

TABLE I. COMPARISON OF VISCOSITIES AND RIGIDITIES OF CORNSTARCH PASTES

(Prepared at 99° C.; measured at 25°)

Starch	Rigidity of	Viscosity of 2.7% Paste		
	5.5% Paste	5 cm.	15 cm.	30 cm.
	<i>Dynes/sq. cm.</i>	<i>Poises</i>		
Popcorn	410	0.45	0.25	0.16
Mandan	325	0.87	0.39	0.25
Yellow Creole	320	0.40	0.20	0.16
Iogent	270	0.36	0.21	0.15
Starch I	220	0.58	0.37	0.25
Reid Yellow Dent	193	0.80	0.34	0.22
Country Gentleman	158	0.18	0.12	0.10
Starch II	120	0.48	0.25	0.19
Waxy maize	0	1.05	0.66	0.51

TABLE II. EFFECT OF MODIFICATION ON THE RIGIDITY OF STARCH PASTES

(5.5% paste; prepared at 99°; measured at 25°)

Starch	Treatment	Rigidity
Commercial starch I	None	240
	Run through homogenizer eleven times	20
Commercial starch II	None	125
	Electrolytic oxidation with 1/10 Cl equivalent	20
	5.5 hours acid treatment by Gore method	0
	Ground in ball mill for 144 hours	12
	Autoclaved for 30 minutes at 120° C.	15

Summary

The apparatus described by Schwedoff for the quantitative measurement of rigidity in gelatin sols has been applied to starch pastes. The method gives reproducible results for a given set of conditions of the paste and is free from instrument constants. The application of rigidity measurements was demonstrated in the comparison of three starches showing extreme variation in physical properties and in the differentiation of nine samples of cornstarch. The assumption that rigidity is dependent upon the condition of the granule membrane is supported by the results of microscopic observation of the granules at various stages of swelling and by rigidity measurements made on several modified starches.

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# Colorimetric Determination of Fluorine with Ferron

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THE difficulties encountered in the quantitative determination of fluorine in rocks and minerals can be pointed out in no better way than by reference to the prolific literature on this subject. From the work of Berzelius (1) in 1816 to that of Stevens (9) in 1936—a period of 120 years—there have been published more than twenty methods and modifications thereof relating to the determination of fluorine and embracing gravimetric, volumetric, colorimetric, and nephelometric methods of analysis. As a review of the literature was made by Stevens (9), further efforts in that direction are unnecessary. However, Steiger's (7) method as modified by Merwin (6) is the most widely used in the analysis of rocks and the Hoffman-Lundell (5) lead chlorofluoride procedure is probably employed more than any other where high percentages of fluorine, characteristic of some minerals, are to be determined.

The method herein described consists in matching in a comparison solution the yellowish hue of green produced by the reaction of fluorine in the unknown solution on the ferron-iron reagent.

## The Ferron-Iron Reagent

Ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) was described by Yoe (11) in 1932 as a colorimetric reagent for ferric iron. In using this compound as a reagent for fluorine, a saturated water solution is combined with a water solution of ferric chloride and hydrochloric acid. The proportions of ferron, ferric chloride, and hydrochloric acid finally decided on were the result of some nineteen attempts to produce a sensitive and stable fluorine reagent. When the iron content was too low, the green color was too weak, and conversely, when more iron than necessary was in the solution, the color was darker than desired. Hydrochloric acid was found to be the best of the three acids tried in the reagent; sulfuric acid causes a partial discharge of color and nitric acid a complete decolorization. As the concentration of hydrochloric acid was increased beyond the desired point, the color became paler, whereas a muddy green resulted from a deficiency of the acid.

The iron as ferric chloride and the hydrochloric acid are contained in a water solution that is 2 *N* to hydrochloric acid and 0.1 *N* to ferric chloride.

The composition of the ferron-iron reagent used is as follows:

	<i>ml.</i>
Saturated water solution of ferron	90
Ferric chloride and hydrochloric acid solution (described above)	10
Distilled water	100

It is believed that this reagent will remain stable indefinitely. No change was noticed after the reagent had stood for 6 months in the light of the laboratory.

## Extraction of Fluorine as Sodium Fluoride

The preliminary extraction of fluorine from a rock follows with few changes that outlined by Hoffman and Lundell (5).

**The colorimetric determination of fluorine, using the ferron-iron reagent herein described, is applicable to a wide range of materials, including rocks and minerals having up to 10 per cent of fluorine and natural waters with a minimum fluorine content of 1 part per million.**

Mix the sample (usually 0.5 gram) with 5.0 grams of sodium carbonate and fuse the mixture in a covered platinum crucible over a Bunsen flame, taking care to keep the cover of the crucible relatively cool. After fusion is attained further heating is needless and may cause a loss of fluorine. Cool and leach overnight with 300 ml. of water in a platinum dish. In the morning bring just to incipient boiling, covering the

dish with a watch glass, and filter hot through a 7-cm. Whatman No. 41 paper. Wash once with hot water and transfer the residue back to the dish with a jet of water. Add water until the volume is approximately 100 ml., boil for about 1 minute, filter through the same paper, and wash well with hot water. Reserve residue A for the silica determination.

To the filtrate in a large platinum dish add a solution containing 1.0 gram of zinc oxide in 30 ml. of hydrochloric acid (1 to 3). Cover with a watch glass and heat to boiling. Allow the precipitate to settle and filter through a 12.5-cm. Whatman No. 41 paper. Wash the platinum dish and the residue on the paper once with hot water. Transfer the residue back to the dish, boil with about 75 ml. of water, filter using the same paper, and finally wash several times with hot water. Reserve residue B also for the silica determination.

Carefully measure the volume of the solution and divide it into two equal parts. To one part add methyl orange indicator and hydrochloric acid (1 to 19) to the end point from a buret. To the other part add the same volume of hydrochloric acid (1 to 19) using no indicator, followed by a solution of 0.5 gram of zinc oxide and 1 gram of ammonium carbonate in 2 ml. of concentrated ammonium hydroxide and 10 ml. of water. Cover the platinum dish with a large glass cover and boil gently until the odor of ammonia is no longer noticed. This requires reducing to a volume of about 75 ml. Add 50 ml. of hot water, stir well, allow the precipitate to settle, filter through a 9-cm. Whatman No. 41 paper, and wash once with hot water. Transfer the precipitate from the paper to the platinum dish, add about 75 ml. of hot water, stir well, and filter through the same paper. Wash once. Residues C, A, and B contain the silica of the sample. Make up the filtrate to 250 ml. This volume will be adjusted during the course of the analysis, so that a 25-ml. aliquot portion will contain from 0.1 to 1.5 mg. of fluorine. When the fluorine content of the sample is less than 0.20 per cent, a 1-gram sample should be used and the final volume after removing residue C reduced to 50 ml.

By fusion with sodium carbonate and subsequent leaching with water only about 60 per cent of the fluorine in phosphate rock is rendered soluble.

## Procedure for Determination of Fluorine

A 25-ml. aliquot portion of the solution containing the fluorine of the sample as the sodium salt is pipetted into a 50-ml. beaker; this will be referred to as the unknown solution. Into another beaker of the same size are measured 25 ml. of a solution having the same pH and the same quantity of sodium chloride per milliliter as the solution containing the fluorine; this will be called the comparison solution. To each beaker 2.00 ml. of the ferron-iron reagent are added. Unless the fluorine content of the sample is very low, a difference in color of the solution will be noticed in the two beakers without resorting to the colorimeter for comparison. The colorimeter used was a Klett top reader of the plunger type, having glass cups 65 mm. deep, with black opaque sides and transparent bottoms.

A 0.02 *N* solution of sodium fluoride is now slowly added from a buret graduated to 0.05 ml. to the greener or comparison solution until the color almost matches that of the unknown. An equal quantity of distilled water is added to the unknown solution in order to maintain the same volume in each of the two beakers.



TABLE I. RESULTS WITH SYNTHETIC SAMPLES						
Sample No.	Weight of Sample	Fluorine Present		Fluorine Found		Error
	Gram	Mg.	%	Mg.	%	
1 <sup>a</sup>	0.1000	10.00	10.00	9.88	9.88	-0.12
2	0.5000	25.00	5.00	24.30	4.86	-0.70
3	0.5000	12.50	2.50	12.80	2.55	+0.30
4	0.5000	5.00	1.00	5.10	1.03	+0.10
5	0.5000	2.50	0.50	2.60	0.52	+0.10
6	0.5000	1.25	0.25	1.35	0.27	+0.10
7	1.0000	1.00	0.100	1.10	0.110	+0.10
8	1.0000	0.50	0.050	0.46	0.046	-0.04
9	1.0000	0.10	0.010	0.14	0.014	+0.04
10 <sup>b</sup>	0.1000	26.41	26.41	25.84	25.84	-0.57
11	0.5000	17.50	3.50	17.35	3.47	-0.15
12	0.5000	6.10	1.22	6.10	1.22	None
13	1.0000	0.90	0.090	1.00	0.100	+0.10
14	1.0000	0.30	0.030	0.40	0.040	+0.10
15 <sup>c</sup>	0.5000	24.30	4.86	24.00	4.80	-0.30

<sup>a</sup> Nos. 1 to 9, inclusive, sodium fluoride in distilled water, prepared by J. J. Fahey.

<sup>b</sup> Nos. 10 to 14, inclusive, sodium fluoride in distilled water, prepared by R. E. Stevens of the Geological Survey.

<sup>c</sup> No. 15, microcline 90 per cent and fluorite 10 per cent, prepared by J. J. Fahey.

TABLE II. COMPARISON OF RESULTS			
Sample No.	Fluorine Found by Other Analysts		Fluorine Found by J. J. Fahey
	%		%
1 <sup>a</sup>	5.72		5.78
2 <sup>b</sup>	7.76		7.52

<sup>a</sup> Bureau of Standards standard sample 91, opal glass.

<sup>b</sup> Lepidolite from San Diego mine, Mesa Grande, Calif. Analysis by R. E. Stevens (8), using Stevens' nephelometric method.

The two cups of the colorimeter are filled with the comparison and the unknown solutions, respectively, and the plungers inserted to the point where the depth of each liquid observed is 50 mm. If the end point has not been reached, the color of the unknown contains more yellow than that of the comparison solution. Repeated additions of the 0.02 N sodium fluoride solution are made to the comparison solution until it attains the same color as the unknown solution in the same volume. From the volume of 0.02 N sodium fluoride solution required to make the match is computed the amount of fluorine in the aliquot portion and in the sample.

A difference in color between the comparison and unknown solutions is evident when the difference in fluorine content of the two solutions is as little as 0.05 mg. If the unknown solution is a natural water containing no more than 1000 parts per million of total solids, the sensitivity is about twice as great as this, making it possible to measure 0.025 mg. of fluorine in the 25-ml. aliquot portion. This greater sensitivity obtained in estimating fluorine in natural waters, over that to be had with rocks, is due to the relatively small quantity of salts in solution in the 25 ml. of the water.

TABLE III. COMPARATIVE RESULTS OBTAINED ON WATERS			
(Ground-water samples from Avoyelles Parish and Rapides Parish, La., obtained from the Water Resources Laboratory, U. S. Geological Survey)			
Water Resources Laboratory No.	Results by M. D. Foster		Results by J. J. Fahey
	P. p. m.		P. p. m.
20,325	7.9		7.5
20,094	4.5		4.6
20,327	1.8		1.9
20,342	1.2		1.1
20,331	0.8		0.8
20,093	5.4		6.1
20,349	0.9		1.2
20,360	1.4		1.5
20,363	2.4		2.3

Evaluation of the Method

Table I gives results obtained on synthetic samples. Samples 1 to 14, inclusive, were treated as aliquot portions of weighed samples, making it possible to compute the concentration of sodium chloride in the aliquot portion and to express the results in percentage.

Table II gives comparisons of results by the method herein described with those obtained by other methods.

Table III gives results obtained on waters by this method compared with those obtained by the Foster ferrithiocyanate method (4). The determination of fluoride in the waters was made without preliminary concentration. Both the comparison solution (distilled water) and the unknown water samples were brought to pH 4.2 before adding the ferron-iron reagent. This acidity is very satisfactory for the determination of fluorine in natural waters.

The percentage error inherent in the ferron-iron colorimetric determination permits its use in the analysis of samples having no more than 10 per cent of fluorine. With rocks or minerals that have higher fluorine contents than this, the absolute error becomes sufficiently great to render the method unsuitable for accurate work. The method as herein described is not sensitive enough to measure accurately less than 1 part per million of fluorine in natural waters. However, it is possible that by using 0.005 N sodium fluoride and a ferron-iron solution that contains less hydrochloric acid than the one used in these determinations this limit can be lowered.

Fluorine Content of Rocks and Minerals

An estimate of the quantity of fluorine likely to be found in rocks and minerals can be obtained from the compilations of Clarke (2) and Wells (10), which record the rock and mineral analyses made in the U. S. Geological Survey from 1880 to 1936. In 1229 mineral analyses reported, there were 18 analyses having more than 10 per cent of fluorine; 27 between 5 and 10 per cent; and 17 from 1 to 5 per cent. In the 3093 rocks analyzed, the highest percentage of fluorine found was 1 per cent. Only 18 samples in 4322 examined had more than 10 per cent of fluorine.

Interfering Elements

It is obvious that colored salts will interfere with obtaining accurate results by this method. However, all such salts, except chromates but including vanadates, as pointed out by Fairchild (3), are removed by controlling the pH in the treatment with zinc oxide outlined in this paper. Chromates, if present in quantities large enough to impart a noticeable color, must be removed. Phosphates are completely taken out by the zinc oxide procedure.

In the analysis of rocks and minerals, it is necessary that the sodium chloride content and the pH of the comparison and unknown solutions be approximately the same, because a large difference would introduce an error.

Summary

A quantitative method for the determination of fluorine, applicable to rocks, minerals, and natural waters, is based on the use of ferron. The green color of the ferron-iron reagent assumes a yellowish hue when fluorine is present. Matching this color with a solution of known fluorine content makes possible an accurate measurement of the percentage of fluorine in the sample.

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# Determination of Cadmium in Silicate Rocks

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FISCHER and Leopoldi (1) have shown that cadmium can be determined in the presence of zinc, lead, and certain other metals by shaking a solution containing 5 per cent of sodium hydroxide with a solution of dithizone in carbon tetrachloride; cadmium goes into the carbon tetrachloride as the dithizonate, whereas zinc and lead remain in the aqueous phase. Use can be made of this behavior in the determination of the minute amounts of cadmium occurring in silicate rocks.

The first steps of the method are practically the same as those in the determination of copper, zinc, and lead in rocks (4). The heavy metals of the sample are isolated by shaking the ammoniacal citrate solution of the decomposed rock with a carbon tetrachloride solution of dithizone. The carbon tetrachloride phase is separated and shaken with 0.01 *N* hydrochloric acid. Zinc, lead, and cadmium dithizonates are thus decomposed, and these metals go into the aqueous phase as the chlorides; copper and cobalt remain in the carbon tetrachloride. Cadmium can then be determined in the aqueous phase by Fischer and Leopoldi's method.

According to Goldschmidt (2) the average cadmium content of magmatic rocks is  $5 \times 10^{-5}$  per cent, although he states that this value is very uncertain. According to I. and W. Noddack (3) the average value is  $2 \times 10^{-5}$  per cent. The few igneous rocks examined in connection with the development of the method here described showed cadmium contents ranging from about 1 to  $2.5 \times 10^{-5}$  per cent, not far from the limit of the method. When a 0.5-gram sample is taken, 0.02 or 0.03 microgram of cadmium, corresponding to  $5 \times 10^{-6}$  per cent, can be detected with certainty.

## Special Reagents

Dithizone, 0.02 per cent (weight by volume) in carbon tetrachloride.

Dithizone, 0.001 per cent (weight by volume) in carbon tetrachloride. One milliliter of this solution shaken with 10 ml. of redistilled water and 2 to 3 ml. of 25 per cent sodium hydroxide solution should yield a colorless carbon tetrachloride layer. This solution should be prepared shortly before use by diluting the stronger dithizone solution.

Sodium citrate, 10 per cent. The solution should be freed from heavy metals by adding a few drops of concentrated ammonium hydroxide to 100 ml. and shaking with successive small portions of 0.01 or 0.02 per cent dithizone in carbon tetrachloride until the latter shows only a very faint pink color.

Sodium hydroxide, 25 grams in 100 ml. of solution.

Hydrochloric acid, approximately 0.01 *N*. Dilute 1 volume of concentrated acid with 1000 of redistilled water. The solution should be shaken with a few milliliters of 0.01 per cent dithizone in carbon tetrachloride and decanted from the latter before use.

## Procedure

Weigh 0.5 gram of rock powder into a platinum dish and add a few milliliters of water, 1 ml. of 70 per cent perchloric acid, and 5 ml. of hydrofluoric acid. Evaporate to dryness, add 0.5 ml. of perchloric acid and a few milliliters of water to the residue, and again evaporate to dryness to expel excess perchloric acid. Moisten the residue with 1 ml. of concentrated hydrochloric acid, add 5 ml. of water, and heat near the boiling point until all soluble matter has been brought into solution.

Add 10 ml. of sodium citrate solution and 0.1 gram of hydroxylamine hydrochloride, neutralize with concentrated ammonium hydroxide using litmus paper, and add 2 drops in excess. If the solution is appreciably turbid at this point, filter through a small filter paper, wash with small portions of water, and ash the paper at a low temperature. Grind the residue with 0.15 to 0.2 gram of sodium carbonate in an agate mortar, transfer the powder to a platinum crucible, and fuse. Leach the melt with water, filter through paper, wash with a few milliliters of water, rinse the insoluble material out of the paper, and heat with dilute hydro-

chloric acid to effect as complete solution as possible. Add 2 or 3 ml. of sodium citrate and a small crystal of hydroxylamine hydrochloride, neutralize with ammonium hydroxide, and add 2 drops in excess.

Extract the main solution (filtrate from any insoluble material) as follows: Add 5 ml. of 0.02 per cent dithizone and shake in a separatory funnel for 0.5 to 1 minute; allow the carbon tetrachloride to settle and draw it off into another separatory funnel. If the carbon tetrachloride drawn off is not greenish, add 2 to 3 ml. more of dithizone to the main solution, shake, draw off, and repeat until the carbon tetrachloride layer shows a greenish color after shaking for 1 minute. In like manner extract the solution resulting from the sodium carbonate fusion, using 1-ml. portions of dithizone in this case.

Combine all the dithizone extracts and shake with 5 ml. of water; discard the water layer. Shake the carbon tetrachloride extract vigorously with 5 ml. of 0.01 *N* hydrochloric acid for 2 minutes. Draw off the carbon tetrachloride layer and repeat the shaking with a fresh 5-ml. portion of 0.01 *N* hydrochloric acid. Combine the acid extracts and discard the carbon tetrachloride. Shake the hydrochloric acid extract with small portions of carbon tetrachloride to remove any colored droplets of carbon tetrachloride in the solution. Finally all droplets of carbon tetrachloride should be separated from the aqueous layer; care should be taken that a film of tetrachloride does not remain on the water surface. The loss of a drop or two of aqueous phase in removing carbon tetrachloride will do no harm.

Transfer the solution to a flat-bottomed glass-stoppered tube, 1.8  $\times$  15 cm., and rinse the separatory funnel with a milliliter or two of water. Prepare a series of standards in similar tubes containing, for example, 0, 0.05, 0.1, 0.15 . . . . microgram of cadmium, dilute with 0.01 *N* hydrochloric acid to the same volume as the unknown, and mix. Add 2.5 ml. of 25 per cent sodium hydroxide solution to each tube and mix. Then add 1.0 ml. of 0.001 per cent dithizone solution and shake vigorously 10 to 15 times. Compare the colors of the carbon tetrachloride layers by viewing the tubes transversely against a white background. The colors fade on standing, and the hue also changes, so that the color comparison should be made immediately after shaking. The hue of the unknown should be the same as that of the standards.

Run a blank on the reagents, taking double the amounts used in the determination itself.

TABLE I. DETERMINATION OF CADMIUM

Sample	Addition	Cd Present 10 <sup>-5</sup> %	Cd Found 10 <sup>-5</sup> %	Error 10 <sup>-5</sup> %
Granodiorite <sup>a</sup>	....	4	4.5	+0.5
	....	4	5	+1
	....	5	5	0
	....	6	5.5	-0.5
	....	7	6.5	-0.5
	0.01% Ni	4	3	-1
	0.02% Ni	4	4.5	+0.5
Extracted <sup>b</sup> solution of granodiorite	....	1.0	0.8	-0.2
	....	2	1.5	-0.5
	....	3	3	0
	0.01% Zn, 0.01% Pb	3	3	0
	0.015% Cu	3	3.5	+0.5
	0.015% Co	3	3	0
	0.04% Ni	3	3	0
	0.01% Ni, 0.2% Mn	4	3	-1

<sup>a</sup> Contained 1 =  $0.5 \times 10^{-5}$ % Cd, 0.006% Zn, 0.004% Cu, and 0.002% Pb.

<sup>b</sup> Solution of granodiorite extracted with dithizone in carbon tetrachloride to remove cadmium originally present, and cadmium then added to the extracted solution.

## Discussion

Some of the results obtained in applying the procedure as described are shown in Table I. There is a tendency for the results to be low, but it is believed that the method is useful for showing the approximate cadmium content of a rock.

Copper, zinc, lead, and cobalt do not interfere, at least not in the amounts that these elements are likely to be en-



countered in igneous rocks. A mixture of 2.5 ml. of 25 per cent sodium hydroxide and 10 ml. of 0.005 per cent pure zinc solution (corresponding to 0.1 per cent of zinc in a 0.5-gram sample) shaken with 1 ml. of 0.001 per cent dithizone solution gave a trace of pink color in the carbon tetrachloride layer which was distinctly less than that produced by 0.05 microgram of cadmium.

Tin, bismuth, silver, and thallium are also without effect in small amounts. Manganese shows a tendency to prevent the complete extraction of cadmium, but this difficulty is overcome by the addition of hydroxylamine hydrochloride.

The element most likely to give trouble is nickel. Nickel dithizonate in carbon tetrachloride solution is partially decomposed by shaking with 0.01 *N* hydrochloric acid, so that more or less nickel will go into the final solution with cadmium. If more than a very small amount of nickel is present in this solution, it will impart a brown color to the carbon tetrachloride layer, the pink color of cadmium dithizonate is then obscured, and the determination becomes impossible. The solution of this difficulty lies in preventing, as far as possible, the extraction of nickel from the ammoniacal citrate solution.

If the solution is made barely ammoniacal most of the nickel will remain in the aqueous phase and all, or nearly all, of the cadmium will be extracted. As much as 0.03 or 0.04 per cent of nickel may be present in the sample without causing difficulty if care is taken to avoid an excess of ammonia. Larger amounts of nickel are likely to cause trouble, so that the method given is not applicable to all rock samples. Moreover, large amounts of any metal extracted by dithizone (copper, zinc, etc.) are undesirable, because the complete removal of cadmium from a large volume of carbon tetrachloride phase by shaking with 10 ml. of 0.01 *N* hydrochloric acid may be difficult. However, in most silicate rocks the quantity of metals extracted by dithizone is small and the method described is adequate.

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## Colorimetric Determination of Nickel As Nickel-Ammonia Complex Ion

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THE rapid development of photoelectric colorimeters and the wide application of colorimetric methods of analysis suggested to the authors the possibility of determining nickel on the basis of the blue color of nickel-ammonia complex ion, the color being measured photoelectrically. Such a method might find some application in steel and ore analysis, being simple and rapid.

### Development of the Method

**APPARATUS AND REAGENTS.** In the proposed method the concentration of nickel was indicated by the spectral transmission of blue nickel-ammonia complex ions. The instrument employed in measuring the transmission was the Yoe photoelectric colorimeter (4).

Special grades of nickel salts low in cobalt and copper were used; all other reagents were of analytical reagent quality. Stock solutions, one each of nickel chloride, nickel nitrate, and nickel sulfate, were made up to contain approximately 5 mg. of nickel per ml., and were standardized gravimetrically with dimethylglyoxime (1). Suitable dilutions of the stock solutions were used in formulating the calibration curve.

**EFFECT OF AMMONIA CONCENTRATION.** A preliminary study of the variations in transmission by nickel-ammonia ions with concentration of ammonia was made in order to determine what concentration of ammonia should be used. From the nickel sulfate solution, two series of standards containing varying amounts of ammonia were prepared; one series had a nickel concentration of 200 mg. per liter and the other 2000 mg. per liter. At an ammonia concentration of 1.5 *N* the solutions were characterized by a blue color and by the complete absence of insoluble basic salt. With increasing concentration of ammonia, the blue complexes gave way

to the violet complexes, the coloration becoming constant at about 2.5 *N* ammonia. Since, in the Yoe instrument as used without color filter, the blue solutions absorb more light than do the violet, they provide the more sensitive means for the determination of nickel. The instrument was therefore calibrated for nickel determination on the basis of the color produced in a solution 1.5 *N* in ammonia.

**EFFECT OF ANIONS.** From the stock solutions of nickel chloride, nickel nitrate, and nickel sulfate, three series of standards were prepared. The ammonia concentration in all cases was 1.5 *N*, but within each series the nickel concentrations varied by convenient intervals. In Figure 1, the plot of values of  $\log R/50$  against nickel concentration shows that the system follows Beer's law only for nickel concentrations up to about 600 mg. per liter. It is obvious that the anion has no influence on the transmission.

**EFFECT OF AMMONIUM SALT.** Since application of this method of analysis would, in all probability, involve making the determination in the presence of ammonium salt, the effect of this factor was investigated. The samples tested covered a nickel concentration range from 50 to 2000 mg. per liter and ammonium salt concentration up to 3.0 *N*. The presence of ammonium salt up to 1.5 *N* had no appreciable effect on the transmission.

**EFFECT OF TIME.** Solutions read at definite time intervals over a period of 150 hours showed no significant variations of transmission with time.

**EFFECT OF COBALT.** Because of the frequent occurrence of cobalt with nickel, a short study was made of the effects of the presence of cobalt on the colorimetric estimation of nickel. Using standardized solutions of cobalt chloride and nickel chloride, a series of solutions was prepared which contained 500 mg. of nickel per liter and varying concentrations



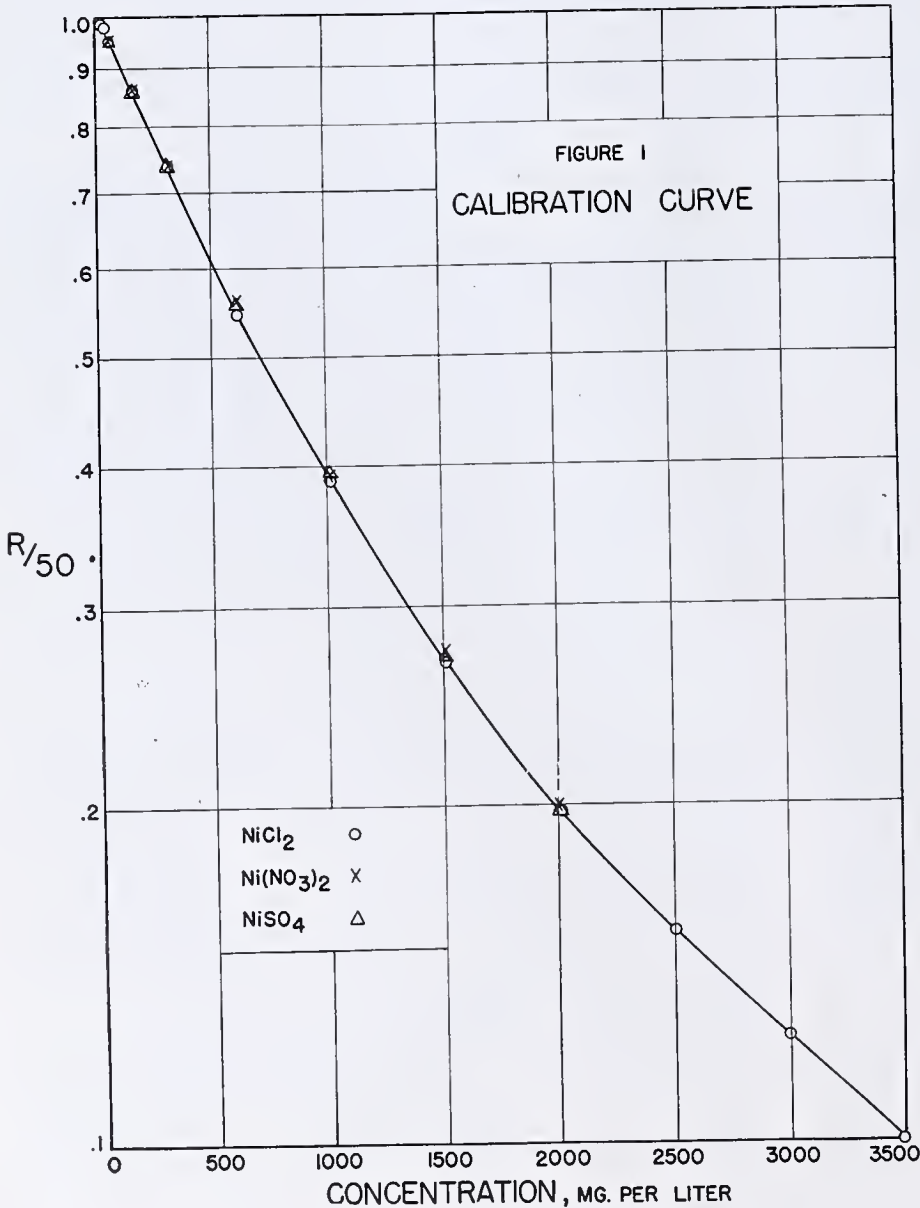
TABLE I. NICKEL FOUND COLORIMETRICALLY AFTER PRECIPITATION AS NICKEL DIMETHYLGLYOXIME

Nickel Taken		Nickel Found		
Mg./l.	R <sup>a</sup>	Gravimetric Mg./l.	Colorimetric from ppt. R	Mg./l.
160	43.5	159.9	43.3	162
200	41.5	200.8	41.0	205
240	39.4	240.3	39.4	240
320	36.2	319.1	36.3	320
400	33.6	399.1	33.5	400
500	30.0	501.4	30.3	497
600	27.6	600.9	27.3	608
800	23.6	800.6	23.2	810

<sup>a</sup> In the tables, R designates colorimeter reading in microamperes

of cobalt in 1.5 N ammonia. Colorimetric readings were made on these solutions at various time intervals. At a cobalt concentration of 50 mg. per liter the blue color representing 500 mg. of nickel per liter was completely obscured by a light brown. Above this concentration of cobalt, the brown color of the solutions increased. After standing approximately 12 hours, the brown color had changed to pink or red, depending upon the concentration of cobalt, and the transmission was still changing after 28 days. The data are represented graphically in Figure 2.

The interference by cobalt could not be eliminated by use of a filter in the instrument. Spectroscopic examination of solutions containing the cobalt-ammonia complex showed that they absorb all wave lengths of the visible spectrum except those in the red; on the other hand, the nickel-ammonia



complex absorbs the red end of the spectrum and transmits the shorter wave lengths. Therefore, when cobalt is present it must be separated unless present in very small, known concentration for which compensation can be made in a corresponding blank of the same age.

TABLE II. COLORIMETRIC DETERMINATION OF NICKEL IN STEEL AFTER SEPARATION OF NICKEL WITH DIMETHYLGLYOXIME

(Volume of solution for colorimetric reading, 100.0 mL.)				
Sample Weight Grams	Colorimetric			Gravimetric
	R	Mg./l.	%	%
1.501	31.0	477	3.18	3.289
1.501	30.9	480	3.20	3.281
1.502	30.9	480	3.20	3.257
1.501	30.5	493	3.29	3.270
1.501	30.5	493	3.29	3.274
1.501	30.2	504	3.36	3.286
1.501	30.3	501	3.33	3.302
1.500	30.4	497	3.31	3.326
1.501	31.0	477	3.18	3.333
1.501	30.3	501	3.33	3.277
Av. 3.27				3.290

Applications of the Method

The determination of nickel colorimetrically as nickel-ammonia complex ion requires the absence of other substances which yield precipitates or colored solutions with ammonia. Since the systematic separation of these interfering constituents is rather laborious, it seemed possible that the well-known quantitative separation of nickel from such ions by dimethylglyoxime in the presence of tartrate, with subsequent decomposition of the nickel dimethylglyoxime thus produced, would provide a means whereby the nickel could be more conveniently isolated in solution suitable for colorimetric determination.

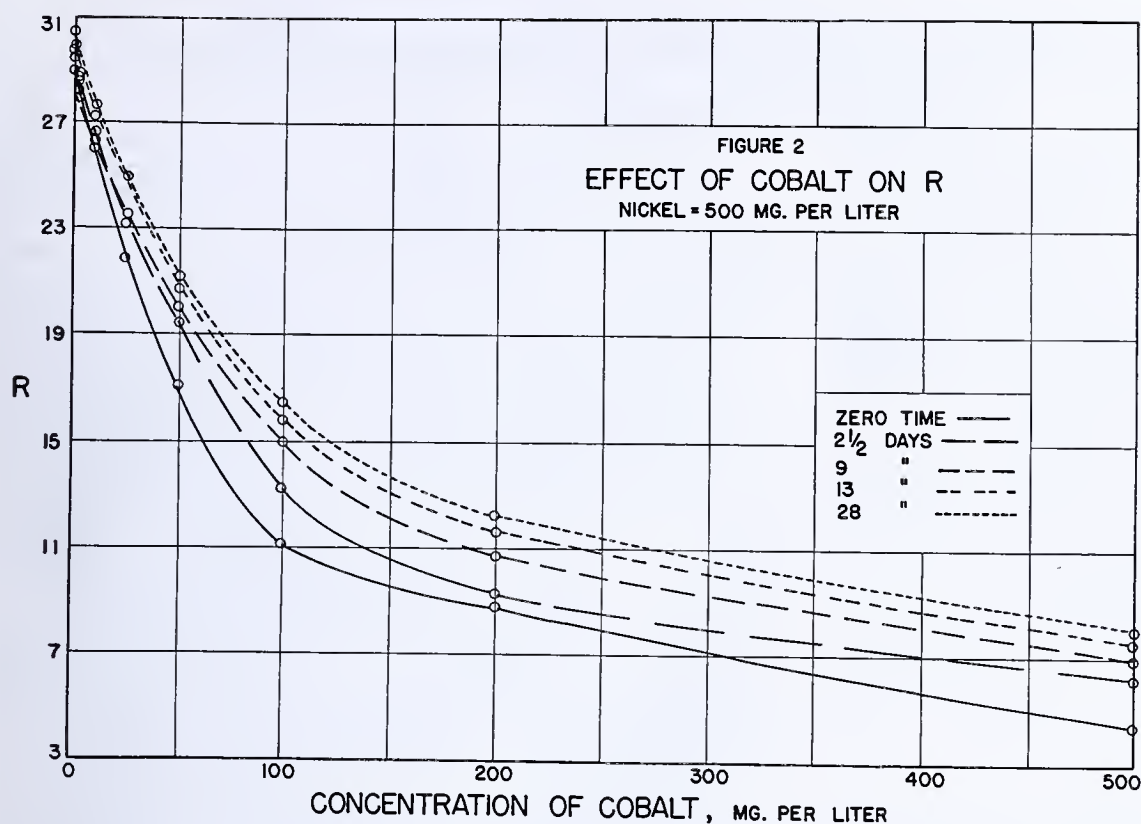
DETERMINATION AFTER SEPARATION AS NICKEL DIMETHYLGLYOXIME. In order to test the method proposed above, a series of standard nickel solutions of varying concentrations was read colorimetrically as nickel-ammonia complex. The nickel in a definite volume of each sample was precipitated with dimethylglyoxime, the precipitate being received in a filtering crucible with fused-in fritted-glass filter disk; to serve as a check on the colorimetric analysis, the nickel dimethylglyoxime precipitate was dried and weighed. This precipitate was then dissolved from the filtering crucible by means of a small amount of concentrated nitric acid, and the acid solution and washings were evaporated to a volume of a few drops. The solution was transferred to a volumetric flask, made up to volume so as to be 1.5 N in ammonia, and then read in the colorimeter.

Blanks prepared from dimethylglyoxime by nitric acid treatment as above gave the same readings as ammonia blanks, indicating the absence of interfering agents in the solution. The results are shown in Table I.

In another series of 7 solutions, each containing 496 mg. of nickel, the nickel found by the above method was 506, 500, 486, 500, 500, 500, and 500 mg.; average, 499 mg.

Samples of nickel steel were analyzed colorimetrically from the nickel dimethylglyoxime precipitate. To serve as a check, these precipitates were dried and weighed before being prepared for colorimetric reading. Results are shown in Table II.





### Discussion of Results

Using the method proposed, the color of nickel-ammonia complex ions is a satisfactory basis for the estimation of nickel. The color system is stable. A concentration of 1.5 *N* ammonia is satisfactory. The presence of ammonium salt affects only slightly the transmission of the solutions. Identical transmissions were obtained in ammoniacal solutions made from the chloride, nitrate, and sulfate of nickel.

Measurements have been made up to a nickel concentration of 4000 mg. per liter. As little as 5 mg. per liter can be detected with certainty. The region of highest sensitivity lies between 500 and 1500 mg. per liter, for in this range the percentage deviation due to the instrument error (0.2 micro-ampere) is at a minimum; within this range the method is accurate to 1 per cent. This method, therefore, compares favorably in accuracy with other colorimetric methods for nickel (2, 3), in which the accuracies range usually from 1 to 5 per cent. Although the intensity of the blue color of nickel-ammonia complex ions is not sufficient to permit visual matching with any degree of accuracy, if the transmission is measured photoelectrically the method is as satisfactory as other colorimetric methods performed visually.

The colorimetric method with ammonia is subject to essentially the same interfering ions as other colorimetric methods for nickel. The separation of nickel from interfering constituents by precipitation with dimethylglyoxime, followed by transposition to nickel-ammonia complex ion for colorimetric estimation, can be accomplished much more simply and rapidly than the removal of interfering ions by precipitations with hydrogen sulfide, ammonia, etc., as required in the thiocarbonate and the dithiooxalate methods.

The use of dimethylglyoxime for accomplishing the separation of nickel, followed by decomposition of the precipitate with nitric acid and the colorimetric measurement of nickel as its ammonia complex, has been applied successfully to the analysis of nickel steel. Although the precision is not high, the average of several determinations agrees well with the average of the gravimetric determinations. From the point at which the nickel dimethylglyoxime precipitate is filtered, the colorimetric method is more rapid than the gravimetric;

it has been the experience of the authors that by the colorimetric procedure a result on the analysis of three to five samples can be obtained in about one half the time required by the gravimetric procedure. The authors are cognizant of the fact that the method proposed requires the constant attention of the analyst during this time, whereas the gravimetric procedure does not.

The nickel dimethylglyoxime precipitate can be decomposed with concentrated hydrochloric acid to give a satisfactory solution for analysis as nickel-ammonia complex, but more difficulty is experienced in dissolving the precipitate from the filter plate with hydrochloric acid than with

nitric acid. Sulfuric acid was found to be unsatisfactory, for during the evaporation of the acid solution there was formed a yellow-green precipitate which was difficultly soluble in water and ammonia. In the use of nitric acid, if evaporation be carried to the separation of solids, the residue is not readily soluble in water or ammonia. This difficulty can be overcome by a second treatment with a small amount of nitric acid, the evaporation being stopped before solids separate.

During the process of calibration of the instrument, and in the subsequent applications of the method, an occasional sample showed a slight turbidity, and most of the samples, including the blank solutions, which were clear by naked-eye observation were seen to scatter light somewhat when placed in the light beam of the instrument. This turbidity could usually be removed by filtration and as a matter of routine in preparing solutions for colorimetric reading they were filtered through Whatman paper No. 50. Traces of any residue left on the filter gave negative tests for nickel.

### Summary

A method has been developed for the colorimetric estimation of nickel as its ammonia complex. The color of the complex is stable, and is very little influenced by added ammonium salt.

The method has been applied to the analysis of nickel in a steel by utilizing dimethylglyoxime to separate the nickel, followed by conversion of the precipitate to nickel-ammonia complex ions for colorimetric determination.

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# Sulfamic Acid in the Separation of the Rare Earths

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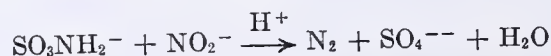
Separation of cerium-free rare earth oxide mixtures into lanthanum and yttrium subgroups is effectively accomplished by conversion to sulfamates and the subsequent treatment of an acidic solution of the sulfamates with sodium nitrite. This method compares favorably with the classical alkali double sulfate procedure.

The sulfamates of lanthanum, neodymium, samarium, and yttrium have been prepared.

THE classical alkali sulfate method is one of the most effective procedures for separating the rare earth members into subgroups. First proposed by Berzelius (2), this method and its numerous modifications are dependent upon the fact that the alkali double sulfates of the lanthanum group—lanthanum, praseodymium, neodymium, and samarium—are almost wholly insoluble in a saturated solution of alkali sulfate, whereas those of the yttrium group—yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium—are soluble. The double alkali sulfates of europium, gadolinium, and terbium (the terbium group) are slightly soluble. Usually the double sulfate separation is employed to divide the rare earths into two fractions containing, respectively, the lanthanum and the yttrium earths. When this is done, the separation takes place at gadolinium, which is found in both subgroups.

The separation into two groups is best accomplished by sifting solid potassium or sodium sulfate into a solution of the rare earth sulfates, nitrates, or chlorides until the neodymium absorption lines become very faint or disappear entirely. The precipitated double sulfates are then composed of fairly pure lanthanum group material, whereas the soluble fraction contains the yttrium earths. However, the separation into the two groups is not sharp, each group invariably being contaminated by the other.

Sulfamates undergo the following reaction when treated with alkali nitrite in acid solution:



An acid solution of rare earth sulfamates upon treatment with sodium nitrite will consequently contain all those ions necessary for the formation of the double alkali sulfates. In other words, the sulfamate ion is a potential source of sulfate ion, which by means of this reaction can be produced *in situ* and at any desired rate. It should, therefore, be possible to effect a separation of the rare earth elements into two groups by means of the above reaction. The experimental work outlined below deals with a study of this possible method for the fractionation of the rare earths. Comparative experiments using the classical method were also carried out. Since cerium is easily removed from a rare earth mixture by oxidation to the tetravalent state, cerium-free materials were used in this study.

## Procedure

One hundred grams of a cerium-free rare earth oxide mixture, composed largely of the lanthanum earths, was treated with a slight excess of sulfamic acid. The solution was diluted to 1500 cc. and the small amount of insoluble material was removed by filtration. The solution of rare earth sulfamates was cooled in an ice bath and solid sodium nitrite was added slowly with constant stirring. A precipitate began to form almost immediately. Sodium nitrite was added until examination of the supernatant liquid with a Hilger constant-deviation spectroscope showed that the 6370 Å. neodymium absorption line had dropped out.

The precipitate was removed by filtration. The filtrate, presumably containing the yttrium earths, was treated with an excess of saturated oxalic acid solution. The precipitated oxalates were filtered, washed with warm water until the filtrate gave no test for sulfate ion, and ignited in an electric muffle furnace. The oxides thus formed were redissolved in nitric acid and the oxalates reprecipitated and reignited.

The precipitate of the insoluble fraction was dissolved in a solution of ammonium acetate (150 grams of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  per 1500 cc. of solution, 4). The oxalates were precipitated and treated in the same manner as those of the soluble fraction.

One hundred grams of the same oxide mixture were fractionated at approximately 90° in the manner described above.

Comparative fractionations by the double sodium sulfate method were made on 100-gram samples of the same rare earth oxide mixture.

A synthetic mixture rich in yttrium members was prepared by mixing intimately 130 grams of yttrium group oxides with 80 grams of cerium-free lanthanum group oxides. One hundred grams of this mixture were fractionated at room temperature by the sulfamic acid procedure.

The mean atomic weights of the original materials and the various fractions were determined from the oxide-oxalate ratio, the oxalate being determined by permanganate titration (3).

The results of the fractions are recorded in Tables I and II.

## Discussion

From the differences in mean atomic weights of the soluble and insoluble fractions, it is readily apparent that the separation of rare earth oxide mixtures into lanthanum and yttrium groups may be carried out as efficiently by the action of nitrous acid upon a solution of sulfamates as by the old classical method, and that the alkali double sulfates formed are less soluble at higher temperatures.

The quantity of materials necessary for at least the same degree of separation is much less by the sulfamate method.

TABLE I. COMPARATIVE FRACTIONATIONS OF MIXTURE RICH IN LANTHANUM GROUP

(Using 100-gram samples of rare earth oxide. Mean atomic weight = 141.8)

Fractionation Method	Reagent Used Grams	Oxides from Insoluble Fraction Grams	Mean Atomic Weight of Insoluble Fraction	Oxides from Soluble Fraction Grams	Mean Atomic Weight of Soluble Fraction
Sulfamate (cold)	82.7	81.4	145.9	13.5	113.0
Sulfamate (hot)	82.7	89.4	142.3	5.4	104.3
	$\text{Na}_2\text{SO}_4$				
Double sulfate (cold)	450.6	84	142.5	7.8	106.3
Double sulfate (hot)	289.9	90.4	142.7	3.5	104.8



TABLE II. FRACTIONATION OF MIXTURE RICH IN YTTRIUM GROUP

	Weight Grams	Mean Atomic Weight
Original	100	117.1
Insoluble fraction	55.1	132.4
Soluble fraction	35.2	104.4

Furthermore, in the classical double sulfate method, a larger amount of sodium sulfate is present in the insoluble fraction and, therefore, this fraction requires more treatment than is necessary when the sulfamate method of separation is used. These are important factors where large quantities of rare earth materials are to be separated into lanthanum and yttrium groups. This new procedure is also of distinct technical interest because of the availability of sulfamic acid (1) as a new industrial chemical at a moderate cost.

**PREPARATION OF SOME RARE EARTH SULFAMATES.** In view of the fact that the method of fractionation described above involves the use of rare earth sulfamates in solution, it was considered desirable to isolate the sulfamates of several typical rare earth metals. The following procedure was used.

Sulfamic acid solution was added to an excess of the rare earth oxide. The mixture was stirred for approximately 0.5 hour and then heated on a steam bath for 1 hour. The reaction mixture was then filtered and concentrated to a small volume on a steam bath. Crystallization of the sulfamates from aqueous solution was ineffective because of their abnormally high solubility in water. Consequently, the concentrated aqueous solutions were gradually dehydrated by shaking with absolute ethanol. Continued treatment of the alcohol-insoluble solution (gummy mass, or solid) with fresh alcohol eventually yielded a powdery material. The sulfamates of lanthanum, neodymium, samarium, and yttrium were prepared in this manner.

Obviously, the amount of water of crystallization in the compounds could have varied considerably. Consequently,

the products were analyzed for their sulfur and rare earth metal content and the ratio of per cent of rare earths to per cent of sulfur was calculated in each case and compared with the theoretical ratio, assuming the starting materials to be 100 per cent pure. The analytical data given in Table III indicate satisfactory concordance between found and calculated values.

The rare earth sulfamates listed in Table III are insoluble in absolute ethyl alcohol, methyl alcohol, acetone, dioxane, pyridine, and liquid ammonia. They decompose slowly at 100° C. to give the corresponding sulfates. In hot aqueous solution the rare earth sulfamates seem to undergo slow hydrolysis.

TABLE III. SULFAMATE VALUES

Formula	Per Cent Sulfur Found	Per Cent Rare Earth Metal Found	Rare Earth-Sulfur Ratio		X = Moles H <sub>2</sub> O
			Obtained	Calculated	
La(SO <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> · XH <sub>2</sub> O	20.26, 20.14	29.14, 29.32	1.44	1.44	2-3
Nd(SO <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> · XH <sub>2</sub> O	20.14, 20.04	31.05, 30.96	1.54	1.50	1-3
Sm(SO <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> · XH <sub>2</sub> O	19.71, 19.76	31.49, 31.66	1.59	1.56	2-3
Y(SO <sub>2</sub> NH <sub>2</sub> ) <sub>3</sub> · XH <sub>2</sub> O	23.49, 23.54	21.21, 21.16	0.90	0.92	1-3

### Acknowledgment

The authors wish to acknowledge their indebtedness to the Grasselli Chemicals Department of E. I. du Pont de Nemours & Company, Inc., for technical sulfamic acid and to B. S. Hopkins for use of the rare earth materials.

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## A Continuous Extraction Diffusion Device

MARTIN MEYER

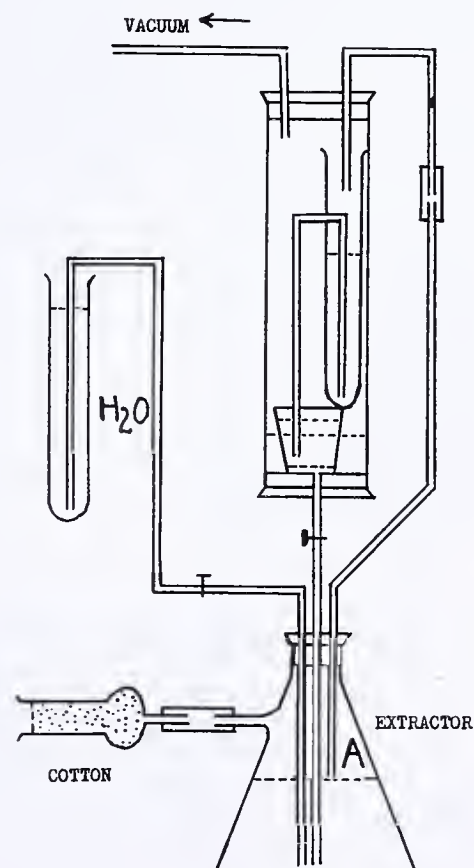
Brooklyn College, Brooklyn, N. Y.

A SIMPLE and continuous diffusion extraction apparatus, for use where a complete extraction is unimportant, is shown in the diagram. It requires a 12-inch section of 3- or 4-inch glass tubing, a Gooch crucible or similar device, a test tube equipped with an internal siphon (which leads into the outside solution, not into the Gooch crucible), a calcium chloride tube packed with cotton, glass tubing, stoppers, a test tube, connectors, and stopcocks as shown.

The solvent is placed in the suction flask and the material to be extracted in the crucible. The apparatus is then closed and the vacuum from an ordinary aspirator is turned on. Operation is controlled and may be adjusted by changing the level of the right-hand tube at A. The effectiveness depends upon the difference in levels at this point.

This device may be made to operate at any desired temperature by removing the vacuum and heating the suction flask. It will then work on pressure instead of vacuum and breathing can be obtained at the top.

The water test tube is designed to compensate for evaporation where the solvent is aqueous, and the cotton removes dirt from the air. The test tube with the siphon in the glass column prevents splashing as the liquid sucks up.





# The Tin-Phosphorus Precipitate in Bronze Analysis

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IT HAS long been known (3, 5) that an insoluble precipitate of the oxides of tin and phosphorus forms in nitric acid solution. This paper reports a study of the tin-phosphorus precipitate and its use in bronze analysis.

## Nature of Precipitate

The nature of the precipitate was first determined by the procedure given below. Table I, Nos. 1 to 8, shows results using tin oxide obtained from an alloy of tin, copper, and zinc

TABLE I. PHOSPHORUS IN PRECIPITATE								
No.	Tin Oxide	Approximate Phosphorus Added	Weight of Oxides		P <sub>2</sub> O <sub>5</sub> in Oxides		Phosphorus in Oxides	
	Gram	Gram	Gram	Gram	Gram	Gram	Gram	Gram
1	0.0123	None	0.0123		None		None	
2	0.0123	0.0054	0.0173	0.0170	0.0050	0.0047	0.0022	0.0021
3	0.0123	0.0108	0.0180	0.0181	0.0058	0.0058	0.0025	0.0025
4	0.0123	0.0162	0.0180	0.0181	0.0058	0.0058	0.0025	0.0025
5	0.0250	0.0162	0.0351	0.0365	0.0101	0.0115	0.0044	0.0050
6	0.0250	0.0216	0.0345	0.0362	0.0095	0.0112	0.0041	0.0049
7	0.0250	0.0260	0.0364	....	0.0114	....	0.0050	....
8	0.0250	0.0314	0.0364	....	0.0114	....	0.0050	....

by the nitric acid method of attack. A series of samples was run in which known amounts of phosphoric acid were added. From 1 gram of bronze 0.0123 gram of tin oxide was obtained. Addition of phosphoric acid to the samples (Nos. 2 to 4) increased the weight of precipitates to a constant value, 0.0181 gram. Even though as much as 0.0162 gram of phosphorus was present, not more than 0.0181 gram of precipitate, containing only 0.0025 gram of phosphorus, could be obtained.

With a pure tin oxide weighing about 0.0250 gram (Nos. 5 to 8) samples treated as above gave increasing weights until 0.0364 gram of oxide was obtained. Though as much as 0.0314 gram of phosphorus was present, not more than 0.0050 gram could be found in the precipitate.

Thus a precipitate of tin oxide and phosphoric oxide is easily obtained in constant proportions. This compound is stannyl phosphate, 2(SnO<sub>2</sub>).P<sub>2</sub>O<sub>5</sub> or (SnO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, containing 53.6 per cent of tin.

Table I explains statements in the literature that the tin-phosphorus precipitate is of variable composition. For example, in Nos. 5 and 6, although more than the necessary 0.0050 gram of phosphoric acid was present, the weight of precipitate varied from 0.0351 to 0.0364 gram, and contained 0.0044 to 0.0050 gram of phosphorus. This means that a precipitate of constant proportions will not be found (under the conditions of this procedure) unless there is present a minimum of 10 mg. of phosphorus for each 10 mg. of tin, and 20 mg. of phosphorus for 20 mg. of tin in the bronze to be analyzed.

## Procedure

Place 1 gram of bronze in a 50-cc. beaker (containing the phosphoric acid) and add 7 cc. of concentrated nitric acid. Allow the mixture to digest on a steam bath for about 20 minutes, then dilute to about 50 cc. with hot water. After about 1.5 hours filter off the tin-phosphorus oxide on a 9-cm. No. 40 Whatman paper, containing paper pulp, wash with a hot (1 + 99 cc.) nitric acid solution, place the paper in a crucible, and dry on a hot plate. Completely burn off the carbon at about 600° C. and ignite at about 800° C.

To determine phosphorus in the tin oxide precipitate, fuse with sodium peroxide, leach out with water, acidify with nitric acid,

and add 6 cc. in excess. Add 2 cc. of concentrated hydrochloric acid, heat to solution, and precipitate the phosphorus with molybdate (4).

While phosphorus completely removed the tin from solution as phosphate, the reverse is not true. For example, Bureau of Standards No. 63, which contains 9.91 per cent of tin, removed 0.58 per cent of phosphorus from solution, but left 0.04 per cent in the filtrate (No. 14). The analytical method (1) of the American Society for Testing Materials for gun metal suggests the empirical factor of "two thirds" as the amount of the phosphorus which will probably be found in the tin precipitate, if the bronze originally contained less than 0.2 per cent of phosphorus. The authors' results show that about 90 per cent of the phosphorus will be found in the precipitate (Nos. 9 to 14, Table II) when the tin is 7 per cent or more.

When a bronze containing up to 2 per cent of tin and some phosphorus is to be determined gravimetrically, the analyst has the choice of using an empirical factor for the phosphorus; of determining the phosphorus in the precipitate exactly, as by peroxide fusion; of determining the tin, usually volumetrically; or of precipitating stannyl phosphate, factor 0.536. Precipitation as stannyl phosphate has the advantage of speed and accuracy in routine analysis.

TABLE II. PHOSPHORUS IN PRECIPITATE				
No.	Weight of Total Oxides	Phosphorus in Precipitate		Phosphorus in Filtrate
	Gram	Gram	%	Gram
9	0.1535	0.0015	94	0.0001
10	0.1273	0.0017	90	0.0002
11	0.1273	0.0011	92	0.0001
12	0.1074	0.0037	90	0.0004
13	0.1147	0.0050	93	0.0004
14	0.1491	0.0058	94	0.0004

TABLE III. TIN			
No.	Tin Taken <sup>a</sup>	Phosphorus Present	Tin Found <sup>b</sup>
	Gram	Gram	Gram
15	0.0200	0.0125	0.0198
16	0.0200	0.0250	0.0210, 0.0210
17	0.0200	0.0370	0.0204, 0.0205
18	0.0200	0.0600	0.0217

<sup>a</sup> Identical samples, 2% Sn, 6.6% Pb.  
<sup>b</sup> As (SnO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.

## Discussion

It is known that iron prevents the quantitative separation of tin as oxide in the routine nitric acid method for bronze. Accordingly, a bronze containing 3 per cent of iron and 8 per cent of aluminum was mixed with weighed amounts of tin metal. After the usual treatment with nitric and phosphoric acids, it was found that tin could be quantitatively recovered, not as stannyl phosphate, but as the mixed oxides. On the other hand, a sample such as Bureau of Standards No. 62 (0.82 per cent tin and 1.13 per cent iron) gave recoveries which were 0.05 to 0.10 per cent high in tin if calculated as stannyl phosphate. Difficulty was also encountered with a sample high in lead (Nos. 15 to 18, Table III). It is believed that such errors can be rectified. Work must also be done on



the separation of tin and antimony (2, 6) on the possible interference of other metals with tin and on the effect of phosphate in the subsequent analysis of the other elements present. Lastly, bronzes of higher tin content seem to settle so rapidly after nitric-phosphoric acid treatment that sufficient phosphoric oxide is not withdrawn from solution.

### Summary

A study of the tin-phosphorus precipitate in the analysis of bronze has shown that the amount of phosphorus present must equal in weight the tin present to get a precipitate of constant stannic oxide-phosphorus pentoxide ratio. Whereas

phosphorus will remove all the tin from solution, the reverse is not true.

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# A Photometric Method for the Determination of Carbon Dioxide

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IN MANY chemical and biological studies it is convenient to make very frequent determination of the carbon dioxide content of gases. This paper describes a simple photometric method for the rapid determination of carbon dioxide by measuring the change in light transmission of a solution of pH indicator through which the gas is bubbled. Only one gas of known carbon dioxide content is required in order to be able to apply a simple equation to the determination of the carbon dioxide content of gases of unknown composition.

Several workers—e. g., Parker (7) and Fegler and Modzelewski (2)—have used pH indicators to determine carbon dioxide. Most carbon dioxide methods make use of basic

solutions and the consequent accumulation of carbonate in the solution. The present method depends, as did that of Higgins and Marriott (4), upon the equilibrium established between the indicator solution and the gas to be measured. The use of this method in closed and open circuit indirect calorimetry will be described in other papers.

### Apparatus and Method

Methyl red is the pH indicator used in this method. Its pKa is 5.1, being red on the acid and yellow on the alkaline side of this pH. A stock solution is prepared by neutralizing the acid indicator with sodium hydroxide, and dilutions are made from this stock solution to final concentrations ranging from  $0.22 \times 10^{-5}$  to  $1.5 \times 10^{-5}$  gram of methyl red per liter. To these are added a few drops of dilute sodium or potassium hydroxide to bring the excess alkali concentration to something in the neighborhood of  $10^{-4}$  to  $10^{-3}$  molar. These dilutions are made up in liter flasks and calibrated as described below. They were found to remain unaltered over several months. Soft-glass cuvettes with depths ranging from 10 to 25 mm. are used in the apparatus.

The arrangement of apparatus is shown in Figure 1. The photometric colorimeter consists of a wooden box with light-tight hinged lid. Light from a flashlight bulb, *L*, operated at 4 volts from a storage battery illuminates the entire sensitive area of a General Electric blocking layer photoelectric cell, *A*. Between the light source and the photoelectric cell are suitable light filters (Wratten No. 74 and Corning No. 397) and a rack bearing two cuvettes which may be moved into the light path. One cuvette, *S*, is a reference standard and contains methyl red in alkaline solution. The other, *T*, contains methyl red in very dilute bicarbonate solution and is equipped with a bubbling arrangement to permit passage of the unknown gas through it. The solutions are moved into position before the filters by means of the slider, *H*. The practice is to adjust the position of the standard cuvette by means of set screws, *ss*, so that the photoelectric current developed by the light passing through either of the two vessels is the same when the test solution is brought into equilibrium with gas containing no carbon dioxide. The ratio  $I_0/I$  when no carbon dioxide is present, then, is unity.

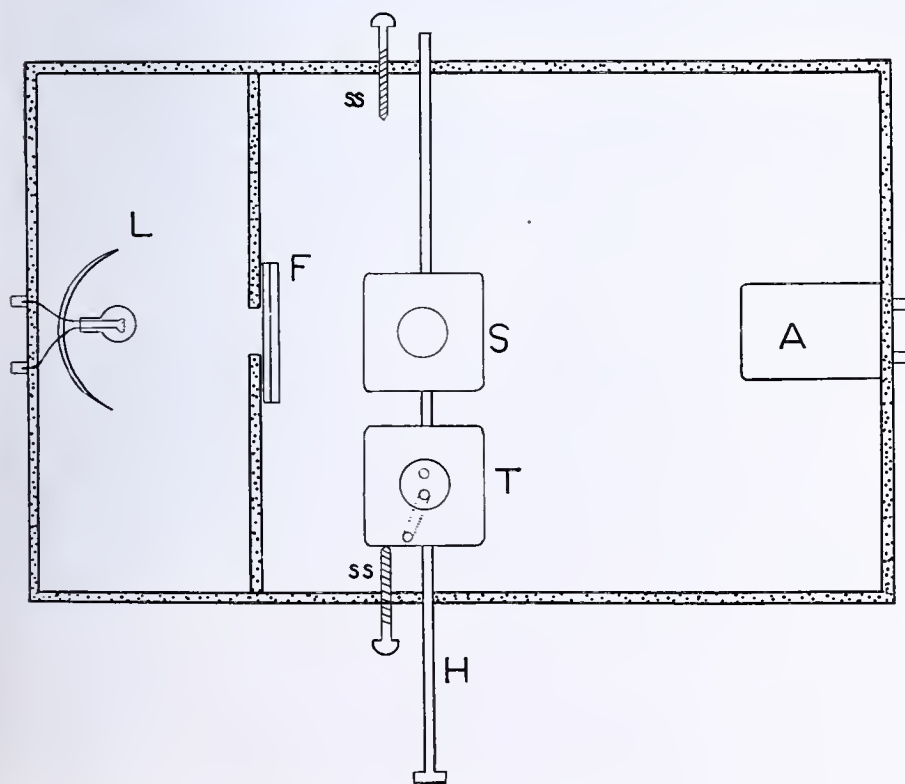


FIGURE 1. DIAGRAM OF APPARATUS

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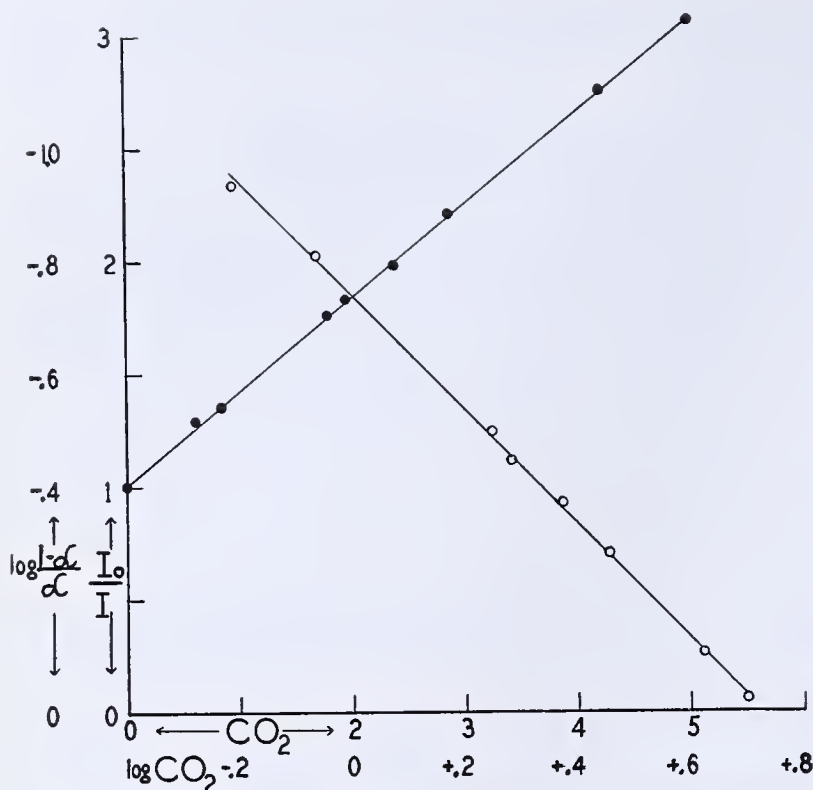


FIGURE 2. PHOTOMETRIC MEASUREMENT OF CARBON DIOXIDE

●.  $I_0/I$  plotted against percentage of carbon dioxide

○.  $\log \text{CO}_2$  plotted against  $\log \frac{1-\alpha}{\alpha}$

Both lines come from data where mixtures of known carbon dioxide content were bubbled through a methyl red solution in which pH and  $I_0/I$  were observed.  $\log \frac{1-\alpha}{\alpha}$  was calculated from pH.

The photoelectric current is measured by observing the deflection of a d'Arsonval galvanometer (Leeds & Northrup, type 2420-C) which has a sensitivity of  $1.8 \times 10^{-8}$  ampere, a resistance of 913 ohms, a critical damping resistance of 18,000 ohms, and a period of 3.2 seconds. A light lever of about 3 meters is employed and the maximum deflection with the standard solution is about 1000 mm.

The following precautions are taken:

The galvanometer deflection is kept within the range where the deflection is directly proportional to the current.

Large temperature changes are avoided.

The photoelectric cell is constantly illuminated.

A low-resistance galvanometer is used, so that the photoelectric current is linear with the light intensity.

Very high concentrations of methyl red are not used because its solubility is less in acid than in alkaline solutions.

The pH is kept from falling below 5.1, the pKa of methyl red.

In making the measurements the flow of gas through the test solution must be momentarily stopped, and in this sense the method is not a continuous one. However, this stoppage is only long enough to permit the gas bubbles to rise to the surface, and the observation is actually made in a very short time. Therefore, the authors feel justified in calling the method a continuous one. The solution serves for repeated analyses over many hours.

The length of time required for the gas to come into equilibrium with the test solutions depends upon the efficacy of the bubbling arrangement. The slow reaction of carbonic acid to carbon dioxide is also involved. Three minutes' bubbling with a single stream of bubbles from a fine capillary will bring 10 cc. of solution into equilibrium with a gas of carbon dioxide content which is widely different from the original.

Any acid- or alkali-forming gas—e. g., sulfur dioxide or ammonia—will interfere with the determination. Such compounds may, however, be removed by suitable absorbing agents before the gas reaches the methyl red solution.

## Gas Mixtures

In order to test the relation between  $I_0/I$  and carbon dioxide content it was necessary to make many gas mixtures of known carbon dioxide tension. This was done by mixing air with gas from a cylinder containing 5 per cent carbon dioxide in nitrogen. These mixtures were usually stored in small cylinders which were evacuated beforehand and made up to a pressure of two atmospheres. The final carbon dioxide content of the mixture was determined indirectly by analyzing the oxygen content of the gas mixture by means of the dropping mercury electrode oxygen method to be described by Baumberger and Mueller. This method of oxygen determination permits of a very accurate and rapid determination of the oxygen per cent of a gas mixture. From the following equations and a knowledge of the oxygen contents of the beginning and final gases, the carbon dioxide content of the final mixture can readily be calculated.

Let  $O_2 = O_2\%$  in air = 20.97%

$O_2' = O_2$  in  $N_2, CO_2, O_2$  cylinder—94.5%  $N_2$ , 5.0%  $CO_2$ , 0.5%  $O_2$

$O_2'' = O_2\%$  in final mixture of gases

$CO_2$  and volume,  $V$ , are similarly indicated

Then

$$V'' = V + V' = 100 \quad (1)$$

$$VO_2 + V'O_2' = V''O_2'' \quad (2)$$

Subtracting 1 from 2

$$V'O_2' - V'O_2 = V''O_2'' - V''O_2 \quad (3)$$

$$V' = \frac{V''(O_2'' - O_2)}{O_2' - O_2} \quad (4)$$

$$CO_2 = \frac{V'CO_2' + V''CO_2''}{V} \quad (5)$$

Equations 3, 4, and 5 are readily solved to give the carbon dioxide tension of the final gas mixture.

The indirect determinations of carbon dioxide by the oxygen dilution method, described above, were checked by means of the Fenn (3) barium hydroxide electrical conductivity method for carbon dioxide and were found to give good agreement. The oxygen dilution method has the advantages of speed and simplicity over the Fenn method.

Often it was convenient to make the gas mixture up quickly in a rubber bag by inflating the bag with compressed air and then adding an amount estimated by the eye from the tank of 5 per cent carbon dioxide in nitrogen. The carbon dioxide content of the gas in the bag was determined by rapidly analyzing for oxygen and making calculations as above. The whole process could be carried out in 5 to 10 minutes. The authors have also allowed the gas to flow continuously from a compressed air system and from the 5 per cent carbon dioxide in nitrogen tank through a Y-tube, through the dropping mercury electrode where the oxygen determination is made, and through the test solution where the ratio  $I_0/I$  is observed. By properly adjusting the flows a mixture of any carbon dioxide content up to 5 per cent can readily be obtained. This is the more convenient method when a series of mixtures is desired.

## Theoretical Basis of the Method

CARBONATE EQUILIBRIUM. The method described depends on the carbonate equilibria, which according to Byck (1) are as follows:



$$[H^+][OH^-] = K_w = 0.54 \times 10^{-14} \text{ (20° C.)} \quad (6)$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_1 = 3.18 \times 10^{-7} \text{ (20° C.)} \quad (7)$$

$$\frac{[H^+][CO_3^{--}]}{[HCO_3^-]} = K_2 = 3.54 \times 10^{-11} \text{ (20° C.)} \quad (8)$$

$$[H^+] = 2[CO_3^{--}] + [HCO_3^-] + [OH^-] \quad (9)$$

$$[H_2CO_3] = ncP \quad (10)$$

$nc$  = Bunsen coefficient = 0.0393

$$[H^+] = \frac{2k_1k_2ncP}{[H^+]^2} + \frac{k_1ncP}{[H^+]} + \frac{K_w}{[H^+]} \quad (11)$$

For pressures of carbon dioxide over  $1 \times 10^{-4}$  atmosphere several of these constants may be neglected, and the equation becomes

$$[H^+] = \sqrt{k_1ncP} \quad (12)$$

These equations apply only to pure water. When the salt of an indicator is present, more and more base is made available for bicarbonate formation as the tension of carbon dioxide increases. The situation is comparable to the two-acid problem of Michaelis (6) which he states is difficult to solve. The pH, observed with the glass electrode, of conductivity water in Pyrex glass in equilibrium with various carbon dioxide mixtures agrees well with the pH calculated by Equation 13.

Since some base is always present—e. g., from the indicator, impure distilled water, or alkali of soft glass—it is convenient to use as simple a system as possible to avoid laborious calculations. This is done by adding enough base so that the total  $HCO_3^-$  concentration is high enough to make negligible both the additional  $HCO_3^-$  from carbonic acid dissociation and the base freed through methyl red association. The buffer equation, 13, satisfies our needs, provided free bicarbonate is at least ten times as large as the two factors mentioned above.

$$pH = -\log k_1 - \log[H_2CO_3] + \log HCO_3^- \quad (13)$$

**PHOTOMETRY.** In the photometric measurements, since the standard is completely transparent to the radiation passing through the filters, its transmission represents the incident light or  $I_0$ . The light transmitted by the test solution corresponds to  $I$ .

When  $I_0/I$  is plotted against the carbon dioxide content of the gas in equilibrium with the test solution, a straight line results (Figure 2). This line has the equation

$$CO_2 = k \left[ \frac{I_0}{I} - 1 \right] \quad (14)$$

The slope of the line and the range of carbon dioxide determination depend upon the concentration of methyl red and alkali, and upon the depth of the cuvette. The authors have used the method to determine carbon dioxide tensions between 0.0 and 8.0 per cent. In practice  $I_0/I$  is plotted against carbon dioxide, and a calibration is accomplished by drawing a straight line through  $CO_2 = 0$ ,  $I_0/I = 1.0$ , and a point determined for a known carbon dioxide tension. Unknown carbon dioxide percentages can then be read directly from the graph from observed values of  $I_0/I$ , or Equation 14 may be applied with the slope of the above line as  $k$ .

The change in concentration of associated methyl red (red form) with change in pH is measured photometrically as described above. The fundamental Beer-Lambert equation is

$$\log \frac{I_0}{I} = kd(1 - \alpha) \quad (15)$$

where  $k$  = extinction coefficient  
 $d$  = depth of cuvette  
 $1 - \alpha$  = red form of methyl red

This equation applies rigidly only when monochromatic light is used. In this method a rather narrow range of wave length is obtained by passing the light through a Corning No. 397 and a Wratten No. 74 filter. Figure 3 shows the region of maximum absorption of both the yellow and the red form of methyl red, and also the absorption of the two filters. It is clear from the figure that the requirement of the Beer-Lambert law is fairly well met. This equation was checked and found to hold by a dilution technique and also by calculating  $1 - \alpha$  from the pH measured by the glass electrode.

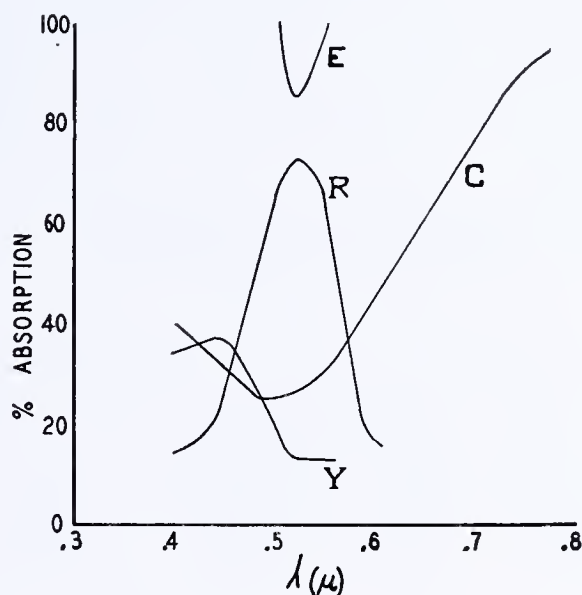


FIGURE 3. ABSORPTION SPECTRA OF METHYL RED AND FILTERS

E. Eastman Kodak Co. filter No. 74e  
 C. Corning filter No. 397  
 R. Red form of indicator  
 Y. Yellow form of indicator

The molecular extinction coefficient (epsilon), in moles per liter and centimeters, was calculated from pH observations using Equation 16, the molar concentration of  $1 - \alpha$ , the depth of the cuvette, and Equation 15. It was found to be  $0.51 \times 10^5$ , which agrees very well with the value in the literature (8) for  $\lambda = 530 m\mu$ .

Since  $k$ , the extinction coefficient, and  $d$ , the depth, remain constant and  $I_0$  and  $I$  are observed,  $1 - \alpha$  may be calculated. Its concentration varies with pH as follows:

$$pH = pK_{a \text{ methyl red}} - \log \frac{1 - \alpha}{\alpha} \quad (16)$$

By combining Equations 13 and 16 it is clear that:

$$CO_2 \propto \frac{1 - \alpha}{\alpha} \quad (17)$$

This relation was tested experimentally in the following manner: The pH and color of an aqueous solution of methyl red were modified by bubbling known carbon dioxide mixtures until equilibria had been reached. The pH was then determined with the glass electrode and  $I_0/I$  was observed. From the pH the value of  $\log \frac{1 - \alpha}{\alpha}$  was calculated with Equation 16, and in Figure 2 it is plotted against  $\log CO_2$ . The resulting straight line proves the validity of Equation 17 which gives the theoretical relationship between carbon dioxide tension and the degree of dissociation of methyl red.



EXPLANATION OF THE UNEXPECTED LINEARITY BETWEEN  $\text{CO}_2$  AND  $I_0/I$ . By combining the Beer-Lambert equation, 15, with the experimentally observed equation, 14, we get

$$\text{CO}_2 \propto 10^{1-\alpha} \quad (18)$$

This relation which is found experimentally is not to be expected a priori.

Equations 17 and 18 would seem incompatible, since one is a hyperbolic and the other a logarithmic relation. However, between certain limits of  $\alpha$  the two curves change at the same rate and both relations can hold. This is shown in Figure 4, where these terms are plotted against  $\alpha$  and against each other. It is seen that in the interval  $1 > \alpha > 0.45$  the hyperbola, when plotted against the logarithm, yields a straight line. Therefore, it is necessary to work with carbon dioxide tensions low enough so that the pH will not fall below 5.1, the pKa of methyl red, in order that  $1-\alpha$  never exceeds 50 per cent of the total concentration of methyl red. For higher tensions of carbon dioxide more free base may be added.

TABLE I. CALCULATION OF PERCENTAGE ERROR OR RATIO WHEN  $I_0$  IS 1000 AND  $I$  IS DETERMINED WITH AN ACCURACY OF ONE SCALE DIVISION

Ratio	$I$	$\frac{I_0}{I} - \frac{I_0}{I-1}$	$\frac{\frac{I_0}{I} - \frac{I_0}{I-1}}{\frac{I_0}{I} - 1} \times 100$
1.1111	900	0.00123	1.215
1.25	800	0.00156	0.62
1.42857	700	0.00204	0.476
1.66667	600	0.00277	0.415
2.0	500	0.00399	0.399
2.5	400	0.00623	0.416
3.33333	300	0.01107	0.473
5.0	200	0.02488	0.622
10.0	100	0.09901	1.10
100.0	10	9.09091	9.10

COMPARISON OF THE SENSITIVITY AND ERROR OF THE pH AND PHOTOMETRIC METHODS. Since a pH indicator is used in this method, it seems logical to consider whether or not the direct measurement of pH of dilute bicarbonate with which carbon dioxide is in equilibrium would be as suitable as the photometric method for determining carbon dioxide. The determination of carbon dioxide by pH has been used by Kauko (5), and by Wilson, Orcutt, and Peterson (9). Such a determination could most conveniently be made with the glass electrode with a sensitivity of about 0.02 pH units. Equation 13 would hold and so:

$$\text{pH} \propto \log \text{CO}_2$$

$$d\text{pH} = 1/\text{CO}_2 \times d\text{CO}_2 \times 0.4343$$

$$d\text{CO}_2 = \frac{d\text{pH} \times \text{CO}_2}{0.4343}$$

$$\text{Sensitivity} = \frac{d\text{CO}_2}{\text{CO}_2} = \frac{d\text{pH} \times \text{CO}_2}{0.4343 \times \text{CO}_2}$$

$$\text{Sensitivity} = 0.02/0.4343 = 2.3\%$$

The error of the photometric method may be determined by calculating the effect on the ratio  $I_0/I$  resulting from the inaccuracy of the measurement of these two factors. The error in the ratio resulting from an error in reading the value can be calculated by Equation 19.

$$\frac{I_0}{I} - \frac{I_0}{I - \text{error}} = \frac{I_0}{I} \quad (19)$$

The authors have made calculations of error in the case where  $I_0$  equals 1000 and  $I$  is measured to within  $\pm 1$ , as in these experiments. These calculations are given in Table I and show that the error resulting from an error in measurement of  $I$  is at a minimum when  $I$  is one half of  $I_0$ . The absolute error in measuring carbon dioxide resulting from this

error in ratio is given in Equation 20 where  $k$  is the same as in Equation 14.

$$k \Delta \frac{I_0}{I} = \text{error in CO}_2 \quad (20)$$

Dividing Equation 20 by Equation 14 and multiplying by 100 we obtain the error in terms of percentage of carbon dioxide present. This error holds for all concentrations of carbon dioxide and dye for any depth of cuvette. It is also the percentage error of the ratio, and is therefore generally applicable to all cases of photometric measurement, provided  $I_0$  equals 1000 times the smallest significant scale division. When the accuracy of measuring  $I$  and  $I_0$  is changed, the error in percentage of ratio changes.

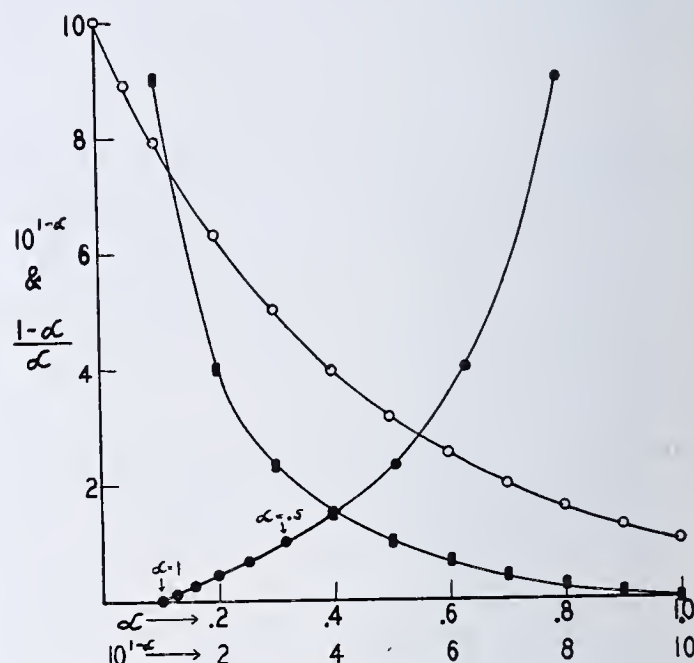


FIGURE 4. LINEARITY BETWEEN  $\text{CO}_2$  AND  $I_0/I$

- .  $\frac{1-\alpha}{\alpha}$  plotted against  $\alpha$
- .  $10^{1-\alpha}$  plotted against  $\alpha$
- .  $\frac{1-\alpha}{\alpha}$  plotted against  $10^{1-\alpha}$ . This curve shows that in the interval  $1 > \alpha > 0.45$  a straight line results from plotting the hyperbola against the logarithm. This accounts for the convenient linear relationship between  $\text{CO}_2$  and  $I_0/I$ .

Table I shows that the error is fairly constant for a wide range of ratios and has a minimal value of  $\pm 0.4$  per cent when  $I_0$  equals 1000 and  $I$  equals 500.

Compared with the pH method, the photometric method is about six times as accurate with the authors' setup.

### Summary

A method is described which permits the continuous photometric determination of carbon dioxide.

A method of making gas mixtures of known composition is described.

A mathematical relationship is derived that simplifies the determination of the concentration of acids by direct measurement of  $I_0/I$ .

A method of calculating the reliability of photometric measurements is developed and applied to the case of carbon dioxide.

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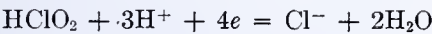
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CONTRIBUTION from the Physiology Laboratory, Stanford University. Work supported in part by a grant from the Rockefeller Foundation and by the National Youth Administration.

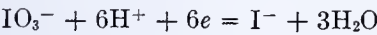
# Volumetric Oxidation of Iodide to Iodate by Sodium Chlorite

L. F. YNTEMA AND THOMAS FLEMING, St. Louis University, St. Louis, Mo.

THE iodide ion may be oxidized to iodate by a chlorite when the iodide solution is buffered with sodium acetate and acetic acid (1). The potential of the couple

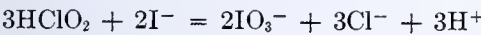


is given by Latimer (4) as 1.56 volts, and that of the couple



as 1.085 volts. There is enough difference in the *E*<sub>0</sub> values so that a quantitative oxidation of iodide to iodate by chlorous acid may be expected. This investigation was undertaken to ascertain under what conditions the reaction may be used for a quantitative volumetric determination of the iodide ion and to examine some of its limitations. Obviously, other oxidizing and reducing agents would interfere.

According to the equation



it is apparent that six equivalents of chlorous acid, measured as an oxidizing agent, will be required to oxidize one mole of iodide. Accordingly, the ratio of equivalents of sodium

chlorite to moles of potassium iodide should be 6 to 1, if the method is valid.

There are few references in the literature to the use of sodium chlorite as a volumetric reagent. Levi and Ghiron (5) employed it for the volumetric determination of permanganate, and Jackson and Parsons (3) developed a method in which it is used in the estimation of sulfite.

### Reagents

The sodium chlorite was obtained from The Mathieson Alkali Works, Inc., by whose analysis it consisted of 98.5 per cent sodium chlorite, with traces of sodium chlorate and sodium hydroxide. All other reagents used were A. R. quality. Distilled water for preparation of solutions was freshly boiled. The sodium chlorite solutions, about 0.13 *N*, were prepared and standardized essentially by the method described by Jackson and Parsons (3). Their observations and those of Levi and Natta (6) concerning the stability of the standardized chlorite solutions were confirmed in this investigation. The potassium iodide solutions, about 0.02 *M*, were standardized by precipitating and weighing the iodide as silver iodide.

### Experimental

Two buffer systems, acetic acid-sodium acetate and monosodium orthophosphate-disodium orthophosphate, were investigated in detail (Tables I and II). The pH measurements were made with a commercial glass electrode assembly. All titrations were carried out at room temperature. A measured volume of the standardized sodium chlorite, about 30 ml., was run from a buret into a flask containing measured volumes of buffer solutions and water. Starch solution was added and the standardized potassium iodide added from a buret. The blue color of the iodine-iodide-starch complex appeared first, and then disappeared as the iodine was oxidized to iodate. It was found that, upon the first addition of iodide, there was an appreciable interval of time before any reaction took place. However, when the first few milliliters of iodide had been oxidized, the reaction proceeded rapidly, provided the acidity was high enough. According to Bray (1) the reaction

TABLE I. ACETATE BUFFER SOLUTIONS

Ratio of Ml., $\frac{2\ M\ HC_2H_3O_2}{2\ M\ NaC_2H_3O_2}$	H <sub>2</sub> O, Ml.	pH	Equiv. of NaClO <sub>2</sub> × 10 <sup>3</sup>	Moles of KI × 10 <sup>3</sup> Amber	Blue	Ratio, Equiv. of NaClO <sub>2</sub> Moles of KI	Average Ratio	Ratio Blue	
$\frac{0.5}{9.5}$	25	..	4.70	0.784	0.786	6.00	5.99	6.00 (8) <sup>a</sup>	5.97 (8)
$\frac{0.5}{9.5}$	50	..	3.69	0.618	0.620	5.98	5.96	5.98 (5)	5.96 (5)
$\frac{0.5}{9.5}$	100	5.80	3.71	0.620	0.622	5.98	5.96	5.98 (5)	5.95 (5) <sup>b</sup>
$\frac{0.5}{9.5}$	200	..	3.66	0.616	0.620	5.94	5.89	5.95 (2)	5.90 (2) <sup>b,c</sup>
$\frac{1}{9}$	25	..	3.69	0.614	0.617	6.00	5.99	6.00 (4)	5.99 (4)
$\frac{1}{9}$	50	..	3.71	0.618	0.620	5.99	5.97	5.99 (8)	5.97 (8)
$\frac{1}{9}$	100	5.37	4.48	0.746	0.747	6.00	5.99	6.00 (10)	5.98 (10)
$\frac{1}{9}$	200	..	4.25	0.708	0.714	6.01	5.96	6.00 (3)	5.96 (3)
$\frac{2}{8}$	25	..	..	...	...	..	..	....	..... <sup>d,e</sup>
$\frac{2}{8}$	50	..	3.68	0.603	0.611	6.11	6.03	6.08 (2)	6.02 <sup>c</sup> (2) <sup>c,e</sup>
$\frac{2}{8}$	100	5.02	4.25	0.697	0.708	6.10	6.01	6.11 (2)	6.04 (2) <sup>c</sup>
$\frac{2}{8}$	200	..	..	...	...	..	..	....	..... <sup>d</sup>

<sup>a</sup> Number of experiments on which averages are based indicated by digit in parenthesis. <sup>b</sup> Reaction slow. <sup>c</sup> End point not sharp. <sup>d</sup> No end point. <sup>e</sup> ClO<sub>2</sub> evolved.



TABLE II. PHOSPHATE BUFFER SOLUTIONS

Ratio of ML, $\frac{1\ M\ NaH_2PO_4}{1\ M\ Na_2HPO_4}$	H <sub>2</sub> O, ML.	pH	Equiv. of NaClO <sub>2</sub> × 10 <sup>3</sup>	Moles of KI × 10 <sup>3</sup> Amber	Ratio, Blue	Equiv. of NaClO <sub>2</sub> Moles of KI	Average Ratio	Ratio Blue	
$\frac{6}{4}$	25	..	3.67	...	0.611	..	6.01	....	6.01 (4) <sup>a</sup>
$\frac{6}{4}$	50	..	3.68	...	0.617	..	5.96	....	5.95 (2) <sup>a</sup>
$\frac{6}{4}$	100	6.50	3.62	...	0.613	..	5.91	....	5.91 (1) <sup>a</sup>
$\frac{6}{4}$	200	..	..	...	...	..	..	....	.... <sup>b</sup>
$\frac{8}{2}$	25	..	4.22	0.702	0.703	6.01	6.01	6.01 (4) <sup>c</sup>	6.00 (4)
$\frac{8}{2}$	50	..	4.13	0.689	0.690	5.99	5.98	5.99 (4)	5.98 (4)
$\frac{8}{2}$	100	6.08	4.12	0.704	0.706	5.98	5.97	5.98 (4)	5.96 (4)
$\frac{8}{2}$	200	..	4.26	0.714	0.716	5.96	5.95	5.96 (2)	5.94 (2) <sup>a,d</sup>
$\frac{9}{1}$	25	..	4.23	0.700	0.703	6.04	6.02	6.04 (7)	6.02 (7)
$\frac{9}{1}$	50	..	3.73	0.621	0.623	6.01	5.99	6.01 (4)	5.99 (4)
$\frac{9}{1}$	100	5.71	4.23	0.706	0.708	5.99	5.98	5.99 (3)	5.98 (3)
$\frac{9}{1}$	200	..	4.26	0.714	0.721	5.96	5.91	5.96 (3)	5.19 (3) <sup>d</sup>
$\frac{9.5}{0.5}$	25	..	3.66	0.606	0.608	6.04	6.03	6.05 (4)	6.04 (4)
$\frac{9.5}{0.5}$	50	..	3.72	0.615	0.617	6.04	6.03	6.04 (4)	6.02 (4)
$\frac{9.5}{0.5}$	100	5.28	4.23	0.707	0.709	5.99	5.97	5.99 (2)	5.97 (2)
$\frac{9.5}{0.5}$	200	..	4.27	0.715	0.722	5.97	5.92	5.99 (2)	5.92 (2)
$\frac{9.8}{0.2}$	25	..	3.67	0.597	0.604	6.14	6.06	6.13 (2)	6.06 (2) <sup>e</sup>
$\frac{9.8}{0.2}$	50	..	3.70	0.610	0.612	6.07	6.04	6.06 (3)	6.01 (3)
$\frac{9.8}{0.2}$	100	5.06	4.20	0.699	0.703	6.01	5.98	6.01 (2)	5.99 (2)
$\frac{9.8}{0.2}$	200	..	4.23	0.705	0.709	6.00	5.97	5.98 (2)	5.96 (2)
$\frac{10}{0}$	50	..	..	...	...	...	..	....	.... <sup>b,e</sup>
$\frac{10}{0}$	100	..	4.20	0.688	0.591	6.11	5.91	6.11 (1)	5.91 (1) <sup>d,e</sup>
$\frac{10}{0}$	200	..	4.21	0.706	...	5.95	..	5.95 (2)	.... <sup>f</sup>

<sup>a</sup> Reaction slow. <sup>b</sup> No end point. <sup>c</sup> Number of experiments on which averages are based indicated by digit in parenthesis. <sup>d</sup> End point not sharp. <sup>e</sup>  $\text{ClO}_2$  evolved. <sup>f</sup> Amber fades to blue.

is favored by the presence of  $\text{I}_2$ ,  $\text{I}_3^-$ , and  $\text{H}^+$ . When the more alkaline solutions were used, the procedure was followed of adding 4 or 5 ml. of iodide at a time and then agitating until the blue color, first formed, had disappeared. As the end point was approached, the iodide was added a few drops at a time with subsequent shaking.

Under the optimal conditions, two distinct end points were noted, first an amber and then the blue of the starch-iodine complex. The amber end point did not appear in the more alkaline solutions, nor the blue in the more acid. Usually the amber was followed, after the addition of 0.10 ml. of iodide, by the first appearance of blue. Considerable excess, 0.50 ml., was necessary to give an intense blue.

The reverse titration, adding the chlorite to the iodide, was also studied, but consistent results could not be obtained. An excess of chlorite was usually needed to discharge the blue color that formed first. However, it was found possible to back-titrate the excess chlorite with iodide and secure good results.

Another series of experiments was carried out in which

basic zinc salts or zinc oxide were used as buffers. Britton (2) reports about 5.9 as the pH at which basic zinc salts precipitate upon the addition of alkali. Fifteen milliliters of 0.2 M zinc sulfate were diluted with 50 ml. of water and sufficient dilute potassium hydroxide was added to precipitate a small amount of basic zinc sulfate. Such solutions were so alkaline that the reaction proceeded too slowly. Then the procedure was tried of suspending 1 gram of zinc oxide in 50 ml. of water and adding 2 or 3 ml. of 30 per cent acetic acid. The chlorite solution was added and titrated with iodide. When the reaction rate was too slow, 1 or 2 drops of acetic acid were added, immediately causing a discharge of color. When the blue was permanent, after addition of 0.5 ml. of acetic acid, the ratio of chlorite to iodide was 6 to 1. In another series dilute hydrochloric acid (10 per cent) was used instead of acetic acid with equally satisfactory results. This procedure is, however, not so convenient as those using soluble buffers.

In order to determine the influence of nitrates, sulfates, and chlorides on the reaction, a series of determinations (Table III) was carried out. The procedure was the same as that employed in securing the data for Tables I and II, except that an amount of the added substance, to give the indicated molarity at the end point, was dissolved in the buffered solution before addition of the

chlorite. Potassium nitrate or sulfate did not interfere. As potassium chloride retarded the reaction, in each case an excess of iodide was added before a color change took place. The effect of the presence of bromides was also investigated. It was found that free bromine was liberated.

### Discussion

Examination of Tables I and II shows that the reaction is quantitative in properly buffered solutions having a pH of 5.3 to 5.7. The best results were obtained in an acetate solution having a ratio of acetic acid to sodium acetate of 1 to 9. In dilute solutions an excess of iodide was required. When the pH was less than 5.2 there was evolution of chlorine dioxide, and when the pH was greater than 6.0 the reaction proceeded very slowly.

It was found that titration to a blue end point required an excess of iodide. Better results were obtained by taking as an end point the amber which is obtained when starch is added to very dilute iodine solutions.



TABLE III. EFFECT OF NITRATE, SULFATE, AND CHLORIDE IONS  
(50 ml. of H<sub>2</sub>O, 1 ml. of 2 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, and 9 ml. of 2 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)

Concn. of Additions	Equiv. of NaClO <sub>2</sub> × 10 <sup>3</sup>	Moles of KI × 10 <sup>3</sup>		Ratio, Amber	Equiv. of NaClO <sub>2</sub> Moles of KI Blue	Average Ratio	
		Amber	Blue			Amber	Blue
0.2 M KNO <sub>3</sub>	4.13	0.689	0.691	6.00	5.98	6.00 (2) <sup>a</sup>	5.98 (2)
1.0 M KNO <sub>3</sub>	4.13	0.688	0.690	6.00	5.98	6.00 (2)	5.98 (2)
0.2 M K <sub>2</sub> SO <sub>4</sub>	4.14	0.689	0.690	6.01	5.99	6.00 (2)	5.99 (2)
0.2 M KCl	4.47	0.747	0.749	5.98	5.96	5.98 (2)	5.95 (2)
0.5 M KCl	4.38	0.732	0.734	5.98	5.97	5.99 (2)	5.97 (2) <sup>b</sup>
1.0 M KCl	4.15	0.695	0.697	5.98	5.96	5.97 (2)	5.96 (2) <sup>b</sup>

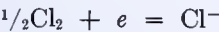
<sup>a</sup> Number of experiments on which averages are based indicated by digit in parenthesis.  
<sup>b</sup> Reaction slow.

TABLE IV. ACCURACY OF METHOD EXPRESSED IN MILLIGRAMS OF DEVIATION

(Solution: 1 ml. of 2 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, 9 ml. of 2 M NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>, and H<sub>2</sub>O as indicated)

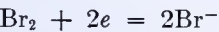
H <sub>2</sub> O	NaClO <sub>2</sub> Taken	I <sup>-</sup> Taken	I <sup>-</sup> Calcd. from NaClO <sub>2</sub>	Deviation
Ml.	Mg.	Mg.	Mg.	Mg.
25	83.3 <sub>5</sub>	77.9 <sub>9</sub>	77.9 <sub>8</sub>	+0.0 <sub>1</sub>
	83.8 <sub>7</sub>	78.4 <sub>3</sub>	78.4 <sub>7</sub>	-0.0 <sub>4</sub>
50	83.7 <sub>9</sub>	78.4 <sub>8</sub>	78.3 <sub>9</sub>	+0.0 <sub>9</sub>
	83.4 <sub>0</sub>	78.0 <sub>4</sub>	78.0 <sub>3</sub>	+0.0 <sub>1</sub>
100	101.1 <sub>7</sub>	94.6 <sub>2</sub>	94.6 <sub>5</sub>	-0.0 <sub>3</sub>
	95.0 <sub>2</sub>	88.8 <sub>7</sub>	88.8 <sub>9</sub>	-0.0 <sub>2</sub>
200	96.1 <sub>0</sub>	89.8 <sub>2</sub>	89.9 <sub>0</sub>	-0.0 <sub>8</sub>
	97.9 <sub>4</sub>	91.7 <sub>2</sub>	91.6 <sub>2</sub>	+0.1 <sub>0</sub>

No interference by small concentrations of chlorides is to be expected, since the potential of the couple



is 1.3583 volts. High concentrations of chloride ion, on the other hand, would retard the reduction of the chlorite.

Since the potential of the couple



is 1.087 volts, a value very close to that of the iodate-iodide, 1.085 volts, the liberation of bromine can be expected.

The observation of Bray (1) that the oxidation of iodides to iodates by chlorite is favored by the presence of H<sup>+</sup>, as well as I<sub>2</sub> and I<sub>3</sub><sup>-</sup>, is confirmed. The reaction is very slow until the first few milliliters of iodide have been oxidized and then is very rapid if the hydrogen-ion concentration is sufficiently high. It is possible that a higher oxidation state of iodine acts as a catalyst for the reaction. Parsons (7)

has suggested that the iodide-iodine pair plays a role in the reaction of chlorites with sulfites.

The accuracy of the method for analytical use is indicated by Table IV, in which some of the data of Table I have been converted from moles and equivalents to milligrams. The deviation of the calculated amount of iodine from the amount taken is within the range of experimental error in each case.

Recommended Procedure

Dissolve a weighed portion of the sample, calculated to contain 0.04 to 0.07 gram of iodide, in freshly boiled distilled water, cooled to room temperature. Buffer with 1 ml. of 2 M acetic acid and 9 ml. of 2 M sodium acetate and add starch solution. Titrate with 0.1 or 0.2 N sodium chlorite solution until a discharge of the blue color indicates that all the iodine, first formed by oxidation of the iodide, has been converted to iodate. Add a small excess of chlorite. Back-titrate with 0.02 M potassium iodide to a permanent amber. One milliliter of 0.2 N sodium chlorite is equivalent to 0.004231 gram of iodine.

Summary

A sodium chlorite solution may be employed for the volumetric determination of iodides in solutions buffered to a pH of 5.3 to 5.7 with either acetates or phosphates. Less satisfactory results were obtained using basic zinc salts as buffers. The reaction involves six equivalents of chlorite for each mole of iodide. Nitrates and sulfates do not interfere. Chlorides retard the reaction and bromides must be absent.

Literature Cited

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Formula for Determining the Viscosity of Latex. A Correction

IN THE authors' paper, "Examination of Rubber Latex and Rubber Latex Compounds. I. Physical Testing Methods" [*IND. ENG. CHEM., Anal. Ed.*, 9, 182-9 (1937)], the following formula on page 187 is in error:

$$\eta' = K_4 \frac{d_{Hg}(w_2P_1 - w_1P_2) + d_1(w_2h_1 - w_1h_2)}{w_2w_1} \frac{t_1t_2}{t_2 - t_1} d_1$$

where

- $\eta'$  = limiting coefficient of viscosity
- $K_4 = \frac{\pi R^4 g}{8 L}$
- $R$  = radius of capillary tube in cm.
- $L$  = length of capillary tube in cm.
- $g$  = acceleration of gravity in cm. per sq. sec
- $d_1$  = density of latex in grams per cc.
- $d_{Hg}$  = density of mercury in grams per cc.
- $P_1$  and  $P_2$  = pneumatic pressures in cm. of mercury

- $h_1$  and  $h_2$  = average heights in cm. of top of latex column above bottom of capillary at pressures  $P_1$  and  $P_2$ , respectively
- $w_1$  and  $w_2$  = weights in grams of liquid delivered at pneumatic pressures  $P_1$  and  $P_2$ , respectively, in times  $t_1$  and  $t_2$ , respectively

This error has been pointed out by B. M. Kedrov [*Caoutchouc and Rubber* (U. S. S. R.), 1938, No. 7, 28-31]. In his paper, Mr. Kedrov includes the correct formula, which is as follows:

$$\eta' = K_4 \frac{(h_1d_1 + P_1d_{Hg}) - (h_2d_1 + P_2d_{Hg})}{w_1t_2 - w_2t_1} t_1t_2d_1$$

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# Determination of Fluorine in Wine

## Modification of the Willard and Winter Method

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**D**URING the last few years the analytical chemist has often been called upon to determine the fluorine content of various food products. It is often necessary to establish whether the fluorine content is below the tolerance of 0.01 grain per pound as required by the United States Food and Drug Administration. Since fluorides and fluosilicates are being used more extensively as insecticides and dusting powders on various crops, the possibility of fluorine contamination is steadily increasing.

The analytical chemist in a commercial laboratory is expected to produce reliable results in the shortest possible time and must have practical methods at his disposal. Numerous contributions on the subject of fluorine determination have appeared in the scientific literature, particularly since the publication of the Willard and Winter method in 1933 (12). Many precautions have been pointed out and a number of valuable improvements have been suggested. If all these suggestions were followed a very lengthy and tedious method would result.

In the course of examining nearly a thousand samples of wine for their fluorine content, the author's laboratories found the following procedure to give the most satisfactory results. The method has been simplified as much as possible, without impairing the accuracy of the results.

### Reagents

Saturated sodium carbonate solution  
Perchloric acid, 60 per cent  
Hydrochloric acid (1 to 20, 5 per cent by volume)  
Hydrochloric acid, 0.1 *N*  
Aqueous solution of sodium alizarin sulfonate, 0.05 per cent  
Ethyl alcohol (or denatured alcohol), 95 per cent  
Thorium nitrate solution, 0.01 *N*  
Standard sodium fluoride solution

### Procedure

Fifty milliliters of wine were measured into a platinum dish, neutralized with a sodium carbonate solution, and evaporated to near dryness on a water bath. The sample was completely freed from moisture by the application of an open flame to the surface of the solids in the dish. (The flame must be kept in continuous motion so as to avoid overheating any portion of the dish, and the heating discontinued as soon as the foaming ceases.) The sample was then burned in a thermostatically controlled electric muffle at a temperature of 525° C.

The ash from the wine was washed from the platinum dish into a 125-ml. distilling flask. Ten milliliters of water had been previously added to the ash for the purpose of dissolving and loosening it from the sides of the dish. The water used for transferring the ash should not exceed 25 ml.

The flask was then connected with a condenser and equipped with a thermometer reaching within 0.5 cm. of the bottom of the flask. Twelve milliliters of 60 per cent perchloric acid were added and the contents steam-distilled by the Willard and Winter (12) method at a temperature between 130° and 140° C. The distillate was collected in a 400-ml. beaker. During the distillation the flask was immersed in an oil bath maintained at about 150° C., as suggested by Reynolds (9). The flow of steam was regulated so as to keep the temperature in the distilling flask as nearly as possible at 135° C. and to collect 200 to 250 ml. in 45 to 60 minutes. If the temperature drops below 130° C. for a short period during the distillation, a larger distillate should be collected. If the rate of distillation is slow, the time should be extended so as to collect a minimum of 200 ml. The flow of steam was regulated by increasing or decreasing the heat under the flask providing the water for the steam distillation.

The distillate was neutralized with a saturated solution of sodium carbonate, so as to make it alkaline to phenolphthalein, and was then evaporated down to a volume of about 10 ml. During the evaporation the temperature of the distillate should not exceed 85° C.

After cooling, the sample was neutralized with a 1 to 20 hydrochloric acid solution, so as just to discharge the color of phenolphthalein. To the colorless solution, 1 ml. of 0.05 per cent aqueous solution of sodium alizarin sulfonate was added, which serves as the indicator in the subsequent titration. This indicator was proposed by Armstrong (2) to replace the zirconium nitrate and alizarin red mixture used in the original Willard and Winter (12) method. The resulting red color was changed to a golden yellow by adding a 0.01 *N* hydrochloric acid solution drop by drop. An excess of only a few drops will interfere with the titration. After this adjustment the solution should have an acidity of about 5.0 pH.

At this point the solution was made up to a volume of 100 ml. and divided into two equal parts, in order to get a double check on the titration. To each aliquot an equal volume (50 ml.) of 95 per cent alcohol was added. The water used for the dilution as well as the alcohol should have an acidity of about 5.0 pH. Denatured alcohol was found to serve the purpose.

The solution was then titrated with a 0.01 *N* solution of thorium nitrate. A small portion of the thorium nitrate solution is used up by the sodium alizarin sulfonate indicator. The correction amounts to 0.1 ml. of 0.01 *N* thorium nitrate for the 0.5 ml. of indicator used in each of the two aliquots.

The titration was conducted by first adding 0.1 ml. of the thorium nitrate solution—the amount required by the indicator. A sharp end point at this time indicated the absence of fluorine. If no end point was reached, the fluorine was titrated by adding the thorium nitrate slowly drop by drop until the end point developed. The sample should be stirred vigorously and be permitted to stand at least 15 seconds after each addition. The volume of thorium nitrate used above 0.1 ml. corresponded to the fluorine in the sample, and the value for each milliliter was obtained from the standardization against a known sodium fluoride solution.

Each aliquot represents 25 ml. of wine. Results may be reported as milligrams of fluorine per liter of wine. By taking the specific gravity of the wine, the results may be calculated as parts per million or grains per pound.

### Ashing Temperature

Since wine contains a considerable amount of sugar, it was necessary to char the sample by applying an open flame to the surface of the solids left after drying on the water bath. If this is not done excessive foaming will result when the sample is introduced into the hot furnace. Samples were burned in thermostatically controlled muffle furnaces at 525° C. This was the lowest temperature at which the resulting carbon could be satisfactorily ashed. The time required for ashing usually is 6 to 12 hours, although some samples require as long as 16 hours.

Experimentation has shown that the temperature of ashing should be kept as low as possible. Winter and Butler (14) ashed their samples at dull red temperature, and Hoskins and Ferris (6) reported a considerable loss of fluorine when the sample was heated up to 800° C. even for a short period of time. One of the experiments conducted in the author's laboratories relative to ashing temperatures consisted in subjecting a solution of sodium carbonate, to which a known amount of sodium fluoride had been added, to temperatures ranging from 450° to 800° C. Results are shown in Table I. A considerable loss of fluorine was observed even at 500° C., only a trace of fluorine being left in the sample which was heated up to 800° C. This indicates the necessity of a suit-



TABLE I. EFFECT OF ASHING TEMPERATURE ON FLUORINE RECOVERY

(Sodium carbonate solution with sodium fluoride added)			
Ashing Temperature ° C.	Fluorine Added Mg.	Fluorine Recovered Mg.	Loss %
450	0.452	0.452	None
500	0.452	0.386	14.6
550	0.452	0.262	42.0
600	0.452	0.196	56.6
650	0.452	0.129	71.4
700	0.452	0.091	80.0
750	0.452	0.063	86.1
800	0.452	Trace	95+

TABLE II. FIXATIVE EFFECT OF WINE ASH

(50 ml. of wine with sodium carbonate and sodium fluoride added)			
Ashing Temperature ° C.	Fluorine Added Mg.	Fluorine Recovered Mg.	Loss %
450	0.452	0.452	None
500	0.452	0.461	None
550	0.452	0.443	2.0
600	0.452	0.452	None
650	0.452	0.452	None
700	0.452	0.424	6.2
750	0.452	0.386	14.6
800	0.452	0.196	56.6

able fixative in the ashing of organic matter when fluorine is to be determined.

### Fixative Effect of Wine Ash

It was found that the ash of wine serves as a fixative for fluorine. While considerable loss of fluorine occurred from dried alkaline sodium fluoride solutions, no loss was observed when the fluorine was added to wine. Table II shows that no loss of fluorine occurred up to 650° C.

An analysis of the ash from a mixture of four different kinds of wine was made to determine the constituents responsible for the fixative properties of wine ash (Table III). This ash represents 0.25 per cent of the wine by weight. It was found to contain about 8 per cent of calcium oxide and about 6 per cent of magnesium oxide. Although aluminum salts possess fixative properties they appeared in only very small amounts.

Dahle (4) used lime in the process of ashing plant material for fluorine determination. Winter (13) suggested the use of magnesium acetate, which was also used by McClure (7). The amounts of fixative used by these authorities were generally high, usually above 0.5 gram.

In making a number of experiments in regard to the fixative values of magnesium oxide and calcium oxide, both of which were found in the wine ash, the author was able to establish that magnesium oxide when used in small amounts has very little fixative effect on fluorine. At least 0.25 gram of magnesium oxide was required to fix 0.45 mg. of fluorine at 600° C., while as little as 0.05 gram of calcium oxide was sufficient to prevent the loss of 0.45 mg. of fluorine at 500° C. as well as 600° C. (Table IV). Slightly high results in the fluorine recovery shown in Table IV were due to the fact that the calcium oxide used in this experiment contained small quantities of fluorine.

The author's investigations show that as long as only small amounts of fluorine are present, the ash of the wine prevents its loss by ashing at 525° C. This makes it possible to simplify the procedure by leaving out the fixative, which can easily be the source of fluorine contamination and lead to an error.

### Distillation

In the original Willard and Winter (12) method 60 per cent perchloric acid was used for the volatilization of fluorine as hydrofluosilicic acid. Since that time perchloric acid has been

used by the majority of investigators. Shuey (11) and others used 95 per cent sulfuric acid, particularly when organic matter was present, because of the explosive properties of perchloric acid in the presence of organic matter. Reynolds (8) suggests the use of phosphoric acid.

The author found 60 per cent perchloric acid to give satisfactory results in the distillation of fluorine from wine ash. A 125-ml. distilling flask was substituted for the conventional 50-ml. Claissen flask. No porous platen or glass beads were introduced into the flask, since wine ash contains a considerable amount of silica. The wine must be thoroughly ashed. Incompletely burned samples cause frothing and consequent carrying over of nonvolatile portions of the ash.

The distillate collected by Willard and Winter (12) was 50 to 75 ml. Reynolds (9) increased the volume to 150 ml.; Hoskins and Ferris (6) reduced the loss of fluorine to a negligible point by collecting 200 ml.; the author collected 200 to

TABLE III. ANALYSIS OF WINE ASH

	%		%
Silicon oxide (SiO <sub>2</sub> )	0.82	Phosphoric acid (P <sub>2</sub> O <sub>5</sub> )	10.35
Aluminum oxide (Al <sub>2</sub> O <sub>3</sub> )	0.25	Chlorine (Cl)	1.15
Iron oxide (Fe <sub>2</sub> O <sub>3</sub> )	0.32	Carbon dioxide (CO <sub>2</sub> )	14.66
Calcium oxide (CaO)	7.81	Manganese (Mn)	Trace
Magnesium oxide (MgO)	6.36	Copper (Cu)	Trace
Potassium oxide (K <sub>2</sub> O)	49.22	Lead (Pb)	Trace
Sodium oxide (Na <sub>2</sub> O)	1.65	Titanium (Ti)	Faint trace
Sulfuric anhydride (SO <sub>3</sub> )	7.27		

TABLE IV. FIXATIVE EFFECT OF CALCIUM OXIDE ON FLUORINE AT 500° AND 600° C.

Fluorine Used Mg.	CaO Added Gram	Fluorine Recovered Mg.	Loss %
Heated for 4 Hours at 500° C.			
0.452	None	0.386	14.6
0.452	0.05	0.461	None
0.452	0.1	0.461	None
0.452	0.25	0.471	None
Heated for 4 Hours at 600° C.			
0.452	None	0.196	56.6
0.452	0.05	0.461	None
0.452	0.1	0.452	None
0.452	0.25	0.461	None

250 ml. The time required for each distillation was from 45 to 60 minutes and the optimum temperature 135° C. If the temperature during the distillation dropped temporarily below 130° C., a larger distillate was collected.

A number of ions, particularly phosphates, sulfates, and chlorides, interfere with the subsequent titration. Reynolds (8), Gilkey (5), and Churchill (3) report interference from the phosphate ion. Churchill (3) was able to overcome the difficulty by a double distillation using first sulfuric and then perchloric acid. Hoskins and Ferris (6) and Armstrong (1) found chlorides to interfere with the titration. This interference was eliminated by McClure (7) and others by adding a silver salt to the distilling flask to fix the chlorides as silver chloride.

Distillates obtained from wine ash as described above, by a single distillation over perchloric acid, were shown to be free from sulfates and phosphates, by making specific tests for those ions on a number of distillates. The use of a 125-ml. distilling flask possibly accounts for this fact. The distillates were found to contain a faint trace of chlorides, but not sufficient to interfere with the titration of fluorine with thorium nitrate.

The distillate, which had been collected in a 400-ml. beaker, was neutralized with a saturated solution of sodium carbonate, so as to make it definitely alkaline to phenolphthalein, and was then evaporated on a hot plate down to about 10 ml. The evaporation should take from 4 to 6 hours, the tempera-



ture not exceeding 85° C. No loss of fluorine due to evaporation in glass containers was observed, as reported by McClure (7).

### Titration

The most delicate step in the determination of fluorine is the adjustment of the acidity previous to the titration. It affects the sharpness of the end point as well as the amount of thorium nitrate required to compensate for the sodium alizarin sulfonate indicator used for the titration.

Rowley and Churchill (10) in making fluorine determinations on aqueous solutions with 0.1 *N* thorium nitrate acidified the solution to a pH of 2.9 to 3.1 before titrating. Hoskins and Ferris (6) used a buffer consisting of sodium hydroxide and chloroacetic acid to control the acidity during the titration at 3.5 pH.

After considerable experimentation in regard to the sharpness of the end point, the amount of indicator to be used, and the optimum acidity for the titration, the following procedure was found to be very satisfactory:

The concentrated distillate was first neutralized with a 1 to 20 hydrochloric acid solution, so as to discharge the color of phenolphthalein. After the addition of 1 ml. of indicator the acidity was carefully adjusted by adding a weak (about 0.01 *N*) hydrochloric acid solution drop by drop until the red color of the indicator changed to a golden yellow. Since the titration with thorium nitrate is extremely sensitive to the acidity of the solution, the addition of the acid should be discontinued just as soon as the golden yellow color is reached.

The solution was then made up to a volume of 100 ml. and divided into two equal parts; 50 ml. of alcohol were added to each of the two aliquots. Titrations made on solutions thus prepared gave a sharp end point and yielded results which were in agreement with added amounts of fluorine.

pH determination made on a large number of solutions prepared as described gave an acidity ranging from pH 4.6 to 5.3 with an average of pH 5.0. The alcohol added before the titration should have the same acidity. Alcohol with excessive acidity should be adjusted to pH 5.0 with sodium carbonate, and perfectly neutral alcohol should be slightly acidified with hydrochloric acid.

Another important factor for a successful titration is the amount of indicator used. Since a portion of the standard thorium nitrate solution is used up by the sodium alizarin sulfonate, the amount of the indicator should be kept constant. In the author's procedure 1 ml. of indicator was used, or 0.5 ml. in each of the two aliquots. This amount required slightly less than 0.1 ml. of 0.01 *N* thorium nitrate, yielding a sharp end point if no fluorine was present. The volume of the standard thorium nitrate used for the titration, less the 0.1 ml. necessary to compensate for the indicator, was in close agreement with added amounts of fluorine.

The titration was conducted on white porcelain or paper. The color of the end point should be the same as is produced by 0.1 ml. of 0.01 *N* thorium nitrate on a solution containing no fluorine, when 0.5 ml. of indicator is used.

No attempt was made to read the volume of thorium nitrate used in the titration closer than 0.05 ml., one drop being added at a time. This naturally makes the fluorine corresponding to 0.05 ml. of standard thorium nitrate solution the smallest amount to be determined by this procedure. One milliliter of a perfectly 0.01 *N* thorium nitrate solution equals 0.19 mg. of fluorine, which makes 0.0095 mg. or 9.5 micrograms of fluorine the limit of accuracy and the smallest amount to be determined.

### Summary

A simplified procedure for the determination of fluorine in wine has been worked out by applying the principles of the Willard and Winter (12) method. It was found that a fixative need not be added previous to the ashing of the sample, since wine ash serves as a fixative for fluorine, thus eliminating a possible chance of error. By the use of a 125-ml. distilling

flask a single steam distillation over perchloric acid yielded a distillate free from interfering ions. A sharp end point was obtained by carefully adjusting the acidity of the solution prior to the titration with thorium nitrate giving consistent and reliable results. While this is not a micromethod, it can be used to determine as little as 0.01 mg. of fluorine.

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## An Efficient Defoaming Agent

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IN CERTAIN food and biological chemical analyses foaming causes difficulties, especially when viscous substances in water are used at room temperatures. In such analytical procedures as the aeration of eggs and meats for the determination of free ammonia in estimating the degree of protein decomposition, paraffin oil is a good defoaming agent, but it does not prevent foaming in the aeration of oysters, clams, and scallops. Capryl alcohol was tried and, although better than paraffin oil, it had the disadvantage of causing a precipitate with Nessler's reagent. Phenyl ether was not as good as capryl alcohol in the prevention of foam and had the same disadvantage in nesslerization. Octyl alcohol (2-ethylhexanol) was tried and found to be a good defoaming agent, having no effect on Nessler's reagent, but was unsatisfactory for a 2-hour run because it volatilized too rapidly, being effective for only from 10 to 15 minutes.

Experiments with octyl alcohol, mixed with various substances which would reduce its vapor tension and possibly increase its defoaming property, resulted successfully with the following mixture:

Hard paraffin	1 part
Heavy paraffin oil (U. S. P. liquid petrolatum)	1 part
Octyl alcohol	2 parts (by volume)

Heat the paraffin and paraffin oil until the paraffin is melted. At this point, stop heating and add the octyl alcohol, mix well, and pour into glass jars or wide-mouthed bottles and allow to cool.

For use in aerometric determinations of free ammonia, 1 gram (this is not critical) in each cylinder works very well. The cylinders used in the authors' work have an inside diameter of 3.5 cm., are 28.5 cm. tall, and should contain about 60-cc. total volume of the mixture being aerated.

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# Determination of Uric Acid in the Mixed Excrements of Birds

## A Modification of the Fritz Differential Extraction Method

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**F**RITZ (1) has discussed the need for an accurate determination of the uric acid in the mixed excrements of birds for the calculation of the digestion coefficient of proteins. He subjected several methods for the determination of uric acid to critical test and was unable to obtain satisfactory results with any of them. He then proposed a new differential extraction method and recommended it because of its simplicity and accuracy.

The differential extraction method is based on the assumption that acidified water extracts the same amount of nitrogen, with the exception of uric acid nitrogen, as does piperidine.

Two equal samples of the excrement (2-gram samples are recommended as a convenient quantity to handle) are treated with 20 ml. of dilute hydrochloric acid (5 parts of concentrated hydrochloric acid and 95 parts of water) and allowed to stand overnight. The samples are filtered, the residues are washed with about 25 ml. of cold water, and the residues and filter papers are transferred to the original beakers. To one of the residues are added about 25 ml. of water and sufficient piperidine to make the sample distinctly alkaline to phenolphthalein. To the other residue are added 25 ml. of 0.1 *N* hydrochloric acid. Both samples are digested in a water bath at 60° C. for 1 hour, and the extracts are filtered off through a layer of Celite on a filter cloth. The residues are washed with equal quantities of cold water until the wash water from the piperidine-extracted material is free from an alkaline reaction. The residues and Celite are transferred to Kjeldahl flasks and total nitrogen is determined. The difference in the nitrogen content of the acid- and piperidine-extracted residues represents the uric acid nitrogen in the sample.

TABLE I. RECOVERY OF URIC ACID ADDED TO A STANDARD SAMPLE OF CHICKEN EXCREMENT

Sample	Uric Acid Added Gram	Uric Acid Found Gram	Recovery of Added Uric Acid %
1	0.1000	0.1017	101.7
2	0.0750	0.0756	100.8
3	0.0500	0.0513	102.6
4	0.0250	0.0258	103.2
5	0.0100	0.0114	114.0
6	0.0150	0.0108	72.0
7	0.0100	0.0099	99.0
8	0.0100	0.0093	93.0
		Av.	98.3

The method as outlined by Fritz was tried on a number of samples of chicken excrement collected and prepared according to the method of St. John and Johnson (2) with fairly satisfactory results. However, with some of the samples difficulty was encountered in obtaining satisfactory duplicate determinations for nitrogen on the piperidine-extracted residues. This difficulty was probably due to improper washing of the alkaline piperidine-extracted residues, the washing process being rather tedious and time-consuming.

### Experimental

In an attempt to improve on the method of filtration and washing of the piperidine-extracted residues, it was found that using 1-gram samples instead of the recommended 2-gram samples and substituting centrifugation for filtration effected considerable saving of time and increased accuracy in the determination. With these changes, the recovery of vary-

ing amounts of uric acid when added to chicken excrement is presented in Table I.

With the modifications used Table I shows that fairly satisfactory results were obtained in the recovery of uric acid added to chicken excrement. However, this is not necessarily evidence that equivalent amounts of nonuric acid nitrogen are extracted from chicken excrement by acidified water and piperidine, as is assumed in the development of the method.

TABLE II. APPARENT VALUES FOR URIC ACID ON URIC ACID-FREE MATERIAL BY THE FRITZ METHOD

Intestinal Contents of Hens	Sample	Nitrogen in Residues Extracted with:		Uric Acid Nitrogen	Uric Acid
		0.1 <i>N</i> HCl %	Piperidine %	%	%
Lower half	1	0.75	0.49	0.26	0.78
	2	0.76	0.49	0.27	0.81
	Av.	0.755	0.490	0.265	0.795
Upper half	1	0.74	0.37	0.37	1.11
	2	0.74	0.36	0.38	1.14
	Av.	0.740	0.365	0.375	1.125

In an effort to verify this assumption some determinations were made on cow feces, which were found to contain no uric acid when an alkaline extract was tested qualitatively with arsenophosphotungstic acid and sodium cyanide. The residue from the acid extraction contained 1.565 per cent of nitrogen whereas the residue from the piperidine extraction contained 1.325 per cent of nitrogen, thus giving a difference of 0.24 per cent of nitrogen which would be considered as uric acid nitrogen by this method. In order to obtain further evidence on this point seven young hens were confined in cages and a composite sample of excrement was collected. The hens were then slaughtered and the contents of two different parts of the small intestine were removed as separate portions. The first portion was removed from the lower half and the second portion from the upper half of the small intestine. The whole excrement and the different portions of the contents of the small intestine were acidified with hydrochloric acid and prepared for analysis.

The material removed from the small intestine of the hens was shown to be free of uric acid when tested colorimetrically with arsenophosphotungstic acid and sodium cyanide. However, when this material was subjected to analysis by the differential extraction method, using 0.1 *N* hydrochloric acid and piperidine, the results shown in Table II were obtained.

It is evident from the data presented in Table II that 0.1 *N* hydrochloric acid and piperidine do not extract equivalent amounts of nitrogen from materials similar to chicken excrement that were shown to be free of uric acid by qualitative tests.

In a study of a number of reagents in which uric acid is soluble, it was found that diethanolamine came nearest to 0.1 *N* hydrochloric acid in extracting nonuric acid nitrogen from cow feces, and at the same time it extracted added uric acid quantitatively. When the concentration of diethanolamine was increased to approximately three times the amount required to make the sample distinctly alkaline to phenolphthalein, there was no reduction in the percentage of nitrogen



in the extracted residue. However, when the concentration of hydrochloric acid was increased from 0.1 to 0.5, 1.0, and 2.0 *N*, respectively, there was a continuous small decrease in the percentage of nitrogen in the acid-extracted residues. *N* hydrochloric acid extracted almost identically the same amount of nitrogen from the sample as diethanolamine.

Time and temperature of digestion and number of washings were varied on both the diethanolamine and hydrochloric acid extractions. Decreasing the time of digestion from 1 hour to 40-, 15-, 10-, and 5-minute periods at 60° C. had no effect on the percentage of residue nitrogen following either the hydrochloric acid or the diethanolamine extractions. Decreasing the temperature of digestion from 60° C. to 50°, 40°, and room temperature (28° C.) for 1 hour caused a continuous slight increase in residual nitrogen after extraction with hydrochloric acid or diethanolamine. When the number of washings was varied very significant results were obtained. With the diethanolamine extraction each washing up to and including the third showed a decided decrease in percentage of residue nitrogen, but further washing was without effect. The wash water was also free of alkalinity to phenolphthalein at the end of the third washing. The residual nitrogen following the acid extraction was constant after the first washing.

TABLE III. URIC ACID VALUES

(Using *N* hydrochloric acid and diethanolamine as extractive reagents for fecal material)

Material	Sample	Nitrogen in Residues Extracted with:		Uric Acid Nitrogen %	Uric Acid %
		<i>N</i> HCl %	Diethanol- amine %		
Cow feces	1	1.57	1.55	0.02	0.06
	2	1.57	1.55	0.02	0.06
	Av.	1.570	1.550	0.020	0.060
Poultry feces Lower half of intestinal contents	1	0.76	0.79	-0.01	-0.03
	2	0.76	0.77	-0.03	-0.09
	Av.	0.760	0.780	-0.020	-0.060
Upper half of intestinal contents	1	0.83	0.80	0.03	0.09
	2	0.84	0.81	0.03	0.09
	Av.	0.835	0.805	0.030	0.090
Normal excrement	1	3.43	0.86	2.57	7.71
	2	3.45	0.84	2.61	7.83
	Av.	3.440	0.850	2.590	7.770

As a result of these experiments diethanolamine and *N* hydrochloric acid were substituted for piperidine and 0.1 *N* hydrochloric acid, respectively; time of digestion at 60° C. was decreased from 1 hour to 10 minutes; the diethanolamine-extracted residue was washed three times with distilled water and the acid-extracted residue was washed once with distilled water, instead of washing both residues until the diethanolamine-extracted residue was free of alkalinity to phenolphthalein. With these changes the method was applied to uric acid-free cow feces, to material taken from the small intestines of young hens, and to whole excrement obtained before the hens were killed, with the results shown in Table III.

These data show that *N* hydrochloric acid and diethanolamine extract equivalent amounts of nonuric acid nitrogen from materials similar to chicken excrement free of uric acid. This is taken as evidence that the difference in the residual nitrogen of chicken excrement samples following extraction with *N* hydrochloric acid and diethanolamine represents the uric acid nitrogen present.

As a result of 15 determinations of uric acid on a standard sample of chicken excrement, the residues following extraction with *N* hydrochloric acid contained from 2.98 to 3.07 with an average of 3.03 per cent of nitrogen. The residues following the diethanolamine extractions contained from 1.09 to 1.11 with an average of 1.10 per cent of nitrogen. The nitrogen value for the diethanolamine-extracted residues sub-

tracted from the corresponding value for the residues extracted with hydrochloric acid is equal to 1.93 per cent of uric acid nitrogen or 5.79 per cent of uric acid.

TABLE IV. RECOVERY OF ADDED URIC ACID BY NEW MODIFIED PROCEDURE

Sample	Uric Acid Added	Added Uric Acid Found	Recovery of Added Uric Acid
	Gram	Gram	%
1	0.0500	0.0501	100.2
2	0.0900	0.0900	100.0
3	0.0450	0.0432	96.0
4	0.0950	0.0954	100.4
5	0.0726	0.0705	96.2
6	0.0521	0.0513	98.5
7	0.1092	0.1101	100.8
8	0.0723	0.0723	100.0
9	0.1043	0.1044	100.1
10	0.0524	0.0510	97.3
11	0.0100	0.0096	96.0
12	0.0100	0.0090	90.0
13	0.0108	0.0099	91.7
14	0.0103	0.0108	104.8
			Av. 98.0

In Table IV are presented data showing recovery of varying amounts of uric acid when added to the standard sample of chicken excrement. Table IV shows the general efficiency of the modified differential extraction method in the recovery of uric acid added to samples of poultry excrement. The poorer individual recoveries may be accounted for to some extent by the smaller amounts of uric acid added in these cases. The general average of 98 per cent for all recoveries is 4.2 per cent higher than that reported by Fritz for his method.

### Recommended Procedure

The chicken excrement is collected and mixed with approximately 1 ml. of 0.45 *N* hydrochloric acid per gram. The acid converts urates to free uric acid and prevents loss of nitrogen present as ammonia. The excess moisture is driven off on a water bath and the sample is then dried to constant weight in an air oven at 100° C. The sample is ground in a Wiley mill to pass a 1-mm. sieve and allowed to come to air-dry condition before analysis. Two 1-gram samples are weighed out and transferred to 100-ml. centrifuge tubes. To one are added about 15 ml. of water and approximately twice as much 10 per cent diethanolamine as is necessary to make the mixture alkaline to phenolphthalein (6 to 8 ml. are usually sufficient) and it is then diluted to 25 ml.; to the other are added 25 ml. of *N* hydrochloric acid. Both samples are digested with frequent stirring in a water bath at 60° C. for 10 minutes.

The samples are removed from the water bath and allowed to cool to room temperature, then thoroughly mixed with the aid of a rubber policeman, and the walls of the tubes washed down with a few milliliters of water. The tubes are centrifuged at about 1500 r. p. m. for about 5 minutes. The supernatant liquid is poured off and the tubes are allowed to drain for a few minutes. The diethanolamine-extracted sample is washed three times, or until the wash water is no longer alkaline to phenolphthalein, with 50 to 70 ml. of distilled water for each wash and centrifuged as before. The hydrochloric acid-extracted sample is washed only once with 50 to 70 ml. of water. After each centrifugation the residues are thoroughly broken up with a stirring rod to ensure efficient and thorough washing. After washing, the residues are transferred to Kjeldahl flasks for total nitrogen determinations. The difference in nitrogen between the *N* hydrochloric acid-extracted residue and the diethanolamine-extracted residue represents the uric acid nitrogen in the sample.

$$\text{Uric acid nitrogen} \times 3 = \text{uric acid}$$

### Summary

A critical study was made of the differential extraction method for the determination of uric acid in chicken excrement.

The method was modified to use 1-gram samples in place of 2-gram samples, and centrifugation in place of filtration. These changes resulted in a considerable saving of time and



a greater accuracy for the determination.  $N$  hydrochloric acid and diethanolamine are recommended as the extractive reagents, since it was shown that  $0.1 N$  hydrochloric acid and piperidine do not extract equivalent amounts of nonuric acid nitrogen from materials similar to chicken excrement free of uric acid.

### Acknowledgment

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ment of Agricultural Chemistry for valuable suggestions made in connection with this investigation.

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# Determination of Electrometric Equivalence Points

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THE staff of Research Project No. 4 of the American Petroleum Institute, in their study (9) of organic matter included in sedimentary rocks, employed a modification of the analytical method of Schollenberger (8). This method of analysis involves the oxidation of the powdered sediment with a predetermined amount of  $0.4 N$  chromic acid, in excess, and the titration of the unreduced acid with  $0.2 N$  ferrous ammonium sulfate solution. The end point in this titration has been determined with the aid of an internal indicator, diphenylamine.

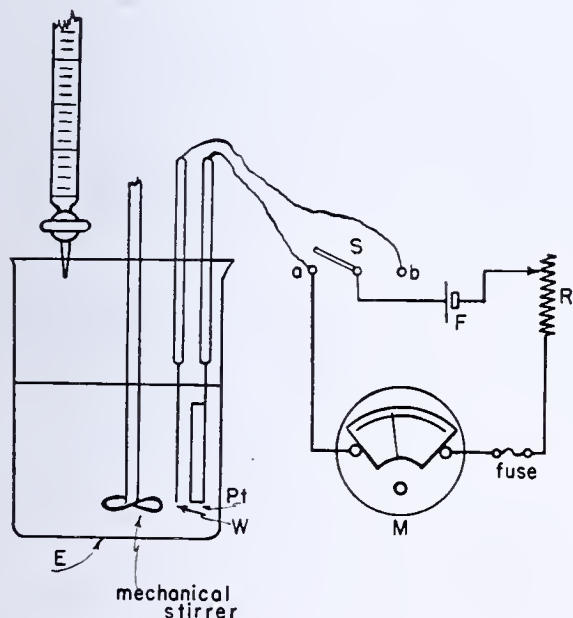


FIGURE 1. SCHEMATIC-PICTORIAL DIAGRAM OF TITRIMETER

- a, b. Poles for two circuits controlled by switch S
- E. Cell composed of electrodes and electrolyte
- F. Dry cell (1.5 volts)
- M. Milliammeter, 0 to 1 milliampere, 1000 ohms per volt sensitivity (Triplett model 221 or 321)
- Pt. Platinum electrode
- R. 1500-ohm, 1-watt, rheostat-type control (wire wound)
- S. Single-pole double-throw knife switch
- W. Tungsten electrode

However, difficulty is encountered in detecting the end point of this particular titration. The suspended particles in the titration vessel may mask or even prevent the observation of the color change, especially with iron-rich sediments. The color of the trivalent chromium is an intense blue, affecting the normal purple hue of the oxidized indicator. More-

over, the indicator in the oxidized condition is a dye, which decomposes gradually and forms a dense, black, tarry deposit around the edges of the solution in the beaker; also, a strong source of light is needed in order to observe the gradual change of the color of the indicator. The indicator has to be added carefully, and a beginner usually requires several days of experience before he becomes adept in detecting the end-point color changes.

These disadvantages are eliminated by electrometric titration. Present methods of detecting equivalence points resolve themselves into two main groups. The first and oldest method involves the use of a sensitive potentiometer. The practice is to balance the potential of cell  $E$  (Figure 1) with a known potential, and, in this way, to determine the greatest potential change for the smallest volume of titrant added (1). It is necessary to plot the potential changes throughout the entire reaction, in order to ascertain the equivalence point.

The second method employs the vacuum-tube voltmeter, and is a comparatively recent development. In this method, the cell potential is measured directly, without drawing any current from the cell. The cell potential is impressed in static charge on the control grid of the vacuum tube, and has a control or Thyatron action on the flow of plate current of the tube. Variations in the plate current are either detected in the first stage or amplified further by a cascade amplifier.

The main point is that in both methods no current is drawn from the cell, so that polarization of the cell is prevented. Polarization causes the formation of gases on both of the electrodes, and halts the action of the cell.

The potentiometric method involves continual manipulation throughout the titration. The vacuum-tube voltmeter, like electron-tube titrimeters, requires a power line source of alternating current of a very good degree of regulation. Moreover, the apparatus needed for both methods is costly.

Consequently, an electrometric method of titration that will overcome these disadvantages is desirable. An inexpensive apparatus was developed which was found to be applicable to electrometric titrimetry to the same extent as the more expensive equipment.

The object of this paper is to explain the operation and applications of this titrimeter, especially its application to simplifying the Schollenberger method of determining organic matter, as employed in the laboratory of Project 4 of the American Petroleum Institute. The instrument gives promise of being useful in other types of titrations, and three others are described in detail in this paper—namely, ferrous



iron-potassium permanganate, ceric cerium-ferrous iron, tetravalent vanadium-potassium permanganate.

### Description of Method

**APPARATUS.** The apparatus employed in this device can be purchased for about \$4. The parts used are schematically represented in Figure 1.

Platinum indicator and tungsten reference electrodes (6, 7, 10) are employed, the surface area of each in contact with the liquid being 15 and 3.7 sq. cm., respectively. Different electrode contact areas will probably prove equally efficient. The meter, *M*, has a sensitivity of 1000 ohms per volt, and requires a 1500-ohm resistor in series with it and a dry cell to drop the current to the proper value of full-scale deflection. Cell *F* is an ordinary 1.5-volt flashlight battery. When the e. m. f. of the cell drops below 1.2 volts, it should be replaced.

**OPERATION.** Since the meter is calibrated in tenths and hundredths milliampere, all readings will be expressed in units of milliamperes times 100.

The first step is to throw the single-pole double-throw switch, *S*, to position *a*. This provides a complete circuit including *M*, *R*, and *F*. The resistance, *R*, is then varied until meter *M* shows full deflection of 1 milliampere. Switch *S* prevents accidental shorting of cell *E*.

Next, the connections from the electrodes to *a* and *b* are arranged so that the e. m. f. of cell *E* will be opposed to that of *F*. In the average oxidimetric reaction, the platinum electrode may be considered the anode and the tungsten electrode the cathode. The switch is then thrown to position *b*.

At this point, a reductant electrolyte will give approximately full-scale deflection (90 to 100 units), because the cell potential will be low, and the needle will drop at the equivalence point, as the cell potential rises when the solution is titrated. For an oxidant electrolyte, the needle will read about half scale (50 units), owing to the fact that the cell e. m. f. resists that of the dry cell, and the needle will rise at the equivalence point, as the potential drops.

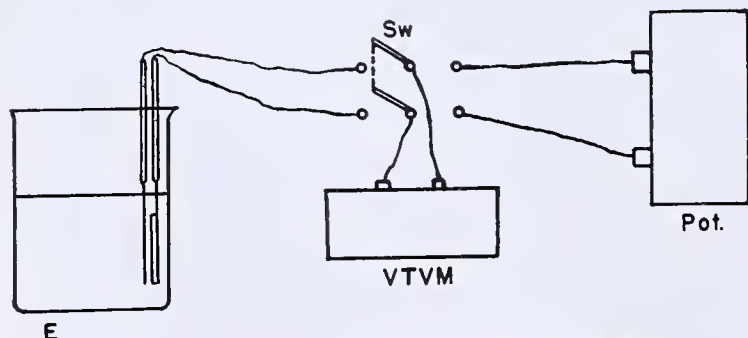


FIGURE 2. ABSOLUTE E. M. F. MEASUREMENT

*E.* Same as cell *E* in Figure 1  
*Pot.* Calibrated potentiometer (0 to 0.8 volt)  
*Sw.* Double-pole double-throw switch (ceramic base knife switch)  
*VTVM.* Vacuum-tube voltmeter (0 to 0.8 volt)

**PRECAUTIONS.** The solutions must be stirred continually throughout titration. The meter circuit should be fused to prevent accidental overloads. The electrodes must be periodically cleaned and sensitized. In order to clean the electrodes, they should be placed in chromic acid cleaning solution, and rinsed with distilled water until free from acid. The platinum electrode should then be ignited in an alcohol flame (not gas), in order to prevent the formation of platinum carbides. The tungsten electrode may be cleaned by polishing with an emery cloth, or better, by dipping momentarily in a bath of molten sodium nitrite and quenching with water before the reaction becomes too vigorous. The electrodes should be left in concentrated chromic acid cleaning solution when not in use, in order to keep them in a sensitive condition.

If the meter swings violently off-scale, when the switch is thrown to position *b*, it is an indication that the cells are acting in series. The leads from cell *E* to contacts *a* and *b* must be reversed.

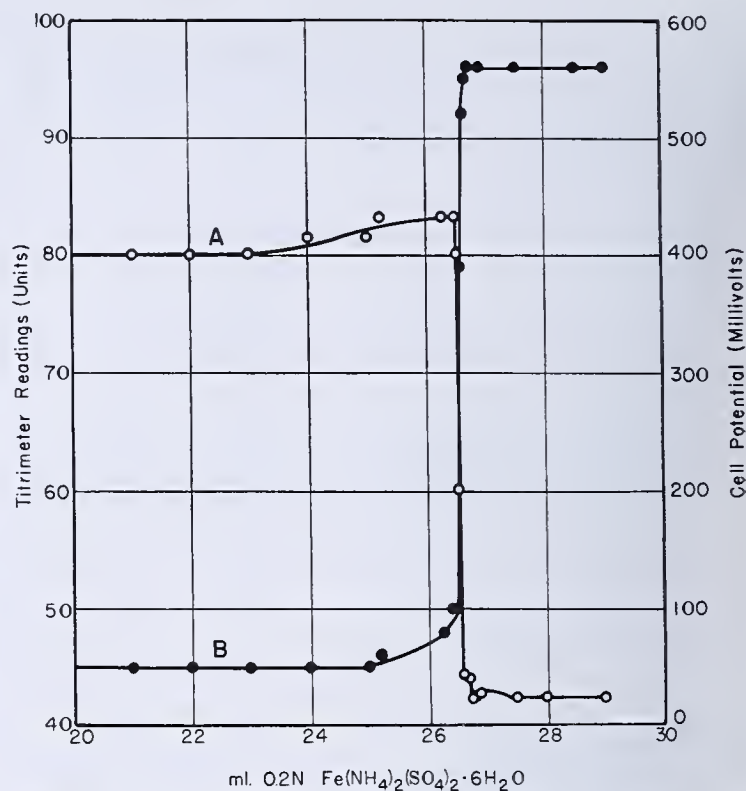


FIGURE 3. TITRATION OF 0.4 N POTASSIUM DICHROMATE WITH 0.2 N FERROUS AMMONIUM SULFATE

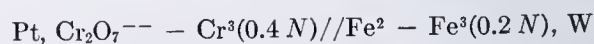
A. Potential variations of cell *E* throughout reaction  
 B. Titrimetric variations of cell *E* throughout reaction

**MEASUREMENT OF POTENTIAL VARIATION IN CELL.** In order to measure the actual potential of any particular cell throughout a titration, the apparatus shown in Figure 2 was employed.

The double-pole double-throw switch, *Sw*, is thrown to the left. This impresses the cell e. m. f. on the vacuum-tube voltmeter, *VTVM*. The reading should be noted. The switch is then thrown to the right, and the potentiometer, *Pot.*, adjusted so that the reading of the vacuum-tube voltmeter is the same as that obtained with the cell. The cell e. m. f. is then read directly or by interpolation, on the potentiometer. In this manner, the cell e. m. f. is accurately obtained without drawing any current that would polarize the cell.

**PROCEDURE IN OXIDIMETRIC TITRIMETRY.** After the titrimeter has been adjusted to full-scale deflection, as described above, the titrant is added gradually, until the needle of the meter flickers perceptibly (about 5 units) from the constant deflection determined by the original cell potential. This shifting of the needle indicates that the equivalence point is within 2 ml. Since the addition of a large amount of titrant, with inadequate stirring of the cell liquid, will cause a sudden deflection regardless of the state of the reaction, the liquid should be continually and rapidly stirred, preferably by a glass propeller as illustrated in Figure 1. The titrant should then be added dropwise; as the equivalence point is approached, each drop will cause a perceptible flicker of the needle, until, at the exact point, a slight excess of the titrant will cause a sudden, large deflection. For example, when dichromate is titrated with ferrous ion (Figure 3, curve B), the deflection is from a reading of 50 units to one of 70 units, for a positive increment of 0.05 ml. of ferrous sulfate solution. At the equivalence point in the reverse reaction, the needle returns to 50 units.

The titration of potassium dichromate with ferrous ammonium sulfate is illustrated in Figure 3. The reaction may be represented schematically as follows:



This reaction is involved in the Schollenberger method for determining organic content of soil. In this reaction, ferrous ammonium sulfate is the titrant. The acid concentration in all cases is 5 per cent by volume of concentrated sulfuric acid (sp. gr. 1.83).



The equivalence point in this reaction is attended by a large potential drop. For a positive increment in volume ( $\Delta V$ ) of 0.05 ml. at the equivalence point, the drop in potential is  $-200$  millivolts and the corresponding titrimeter variation is  $+29$  units. Since a deflection of 5 units is easily noted, 0.01-ml. increment in ferrous ammonium sulfate can be readily detected. Hence, the sensitivity is greater than is experimentally possible to measure with normal volumetric apparatus.

The end points obtained with the use of diphenylamine indicator were observed to differ slightly from the equivalence points, as determined electrometrically. This discrepancy is due to the fact that a concentration of 4 mg. of chromic anhydride per liter of solution is necessary to keep the diphenylamine in the oxidized condition. However, since the control is affected in the same way, the results of titrations are not changed, as is shown by the accordance between the results of titrating 8 samples in the laboratory of Project 4, with diphenylamine and with the electrometric titrimeter (Table I).

TABLE I. TITRATION FIGURES FOR EIGHT SEDIMENTS

Sample	Diphenylamine	Titrimeter
A	3.00	3.07
B	0.73	0.75
C	0.30	0.28
D	1.01	1.00
E	0.75	0.72
F	1.95	1.95
G	1.67	1.67
H	1.42	1.41

**SENSITIVITY.** The sensitivity of the titrimeter varies with individual reactions. With regard to the examples of oxidimetry studied, the maximum sensitivity was found to be 33 millivolts. In order to calculate this maximum sensitivity, the reaction between ferrous ammonium sulfate and potassium dichromate was studied (Figure 3), because the potential changes at the equivalence point were the most pronounced of all those encountered. For an addition ( $\Delta V$ ) of 0.05 ml. of ferrous sulfate at the equivalence point (26.50 to 26.55 ml), the potential changes from 400 to 200 millivolts, or  $-200$  millivolts (curve A). For this same  $\Delta V$ , by projecting the abscissas onto curve B, the titrimeter reading is seen to vary from 50 to 79 units. Since the smallest deflection of the titrimeter that can be readily noted is 5 units, about one sixth of the  $\Delta V$ , or less than 0.01 ml., could be detected in this case. This corresponds to  $200/6$  or 33 millivolts potential change.

If the potential change is very gradual, it will be necessary to plot titrimeter deflections per  $\Delta V$  against  $\Delta V$  (5). The maximum peak of the curve will represent the equivalence point.

**DISCUSSIONS.** The tungsten-platinum bimetallic electrode system has been found to be the most sensitive system which is resistant to the conditions of acidity and oxidation encountered in oxidimetry (3, 10, 11). The platinum electrode is the anode or indicator electrode, and the tungsten is the cathode or reference electrode.

The opposing e.m.f. of the dry cell against that of cell E renders the system sensitive by preventing desensitizing polarization of E. This has been the objection to methods that employ a moving coil meter to indicate potential change. All these methods polarize the cell, even when considerable resistance is inserted in series with the meter. These methods also employ a galvanometer costing more than \$20.

Measurement of the cell potential with a 100-millivolt moving coil meter and multiplying resistor was attempted, but polarization occurred at once, and the potential dropped to zero.

Change in conductance (2) of the cell is not great enough to affect the measurement of the equivalence point with the device described.

## Other Applications

**INDIVIDUAL OXIDIMETRIC REACTIONS.** In order to ascertain whether the titrimeter would find greater applications in the field of electrometric titrations, three reactions were studied: (1) potassium permanganate-ferrous ammonium sulfate, (2) ceric cerium-ferrous ammonium sulfate, and (3) tetravalent vanadium-potassium permanganate.

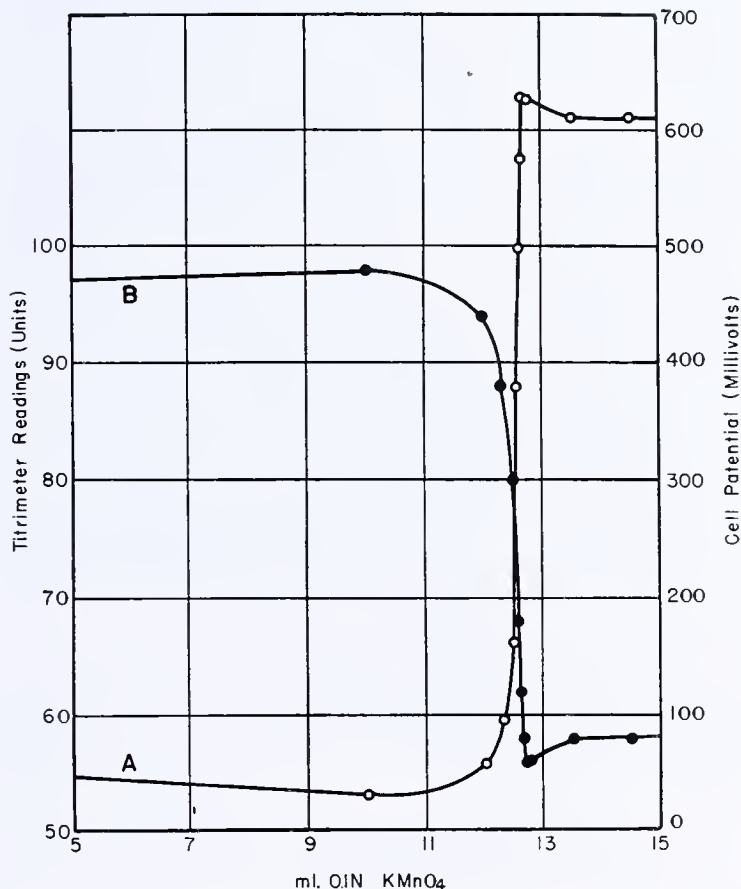


FIGURE 4. TITRATION OF 0.2 N FERROUS AMMONIUM SULFATE WITH 0.1 N POTASSIUM PERMANGANATE

A. Potential variations of cell E throughout reaction  
B. Titrimeter variations throughout reaction

The first reaction was chosen as one very commonly employed in permanganimetry; the second, because there is no very satisfactory color indicator for use with ceric cerium; and the third, because of the very small potential change at the equivalence point, which would be a strict test of the sensitivity of the titrimeter.

The purpose of all the titrations was to plot the potential changes throughout the reaction against those of the titrimeter for the identical reaction, and thus determine the sensitivity and applicability of the instrument. The acid concentration in all the titrations was 5 per cent by volume of concentrated sulfuric acid (sp. gr. 1.83).

The reaction between 0.1 N potassium permanganate and 0.2 N ferrous ammonium sulfate is illustrated in Figure 4. Schematically, the reaction may be represented as follows:

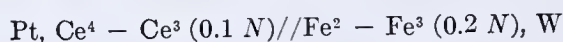


Potassium permanganate is the titrant.

The equivalence point in this reaction is represented by a potential rise of 210 millivolts at the 0.05-ml. increment between 12.50 and 12.55 ml., and is accompanied by a titrimeter variation of  $-12$  units. Thus, an accuracy of 0.02 ml. is possible. The potential drops slightly as the equivalence point is approached, and at the same time the titrimeter reading increases slightly for a proportional variation in the volume of permanganate added. Deflection and potential maxima coincide for given  $\Delta V$  at the equivalence point.



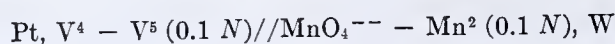
The reaction between 0.1 *N* ceric sulfate and 0.2 *N* ferrous ammonium sulfate is illustrated in Figure 5. Schematically, the reaction may be represented as follows:



In this reaction, ceric sulfate is the titrant.

Maximum titrimeter and potential changes occur at the same point—namely, after the addition of 20.45 ml. of ceric sulfate. The potential rise of 180 millivolts is equivalent to a titrimeter deflection of  $-7$  units. Since deflections of 5 units are readily discernible, it follows that an accuracy of 0.04 ml. of titrant is readily obtainable. The cell potential changes are closely followed by proportional meter deflections.

The reaction between 0.1 *N* tetravalent vanadium and 0.1 *N* potassium permanganate is illustrated in Figure 6. Schematically, the reaction may be represented as follows:



In this reaction, potassium permanganate is the titrant.

The equivalence point is accompanied by a relatively small potential change (4), and occurs between 26.15 and 26.20 ml. The potential change is  $+90$  millivolts. The corresponding titrimeter variation is  $-4$  units. Potential and deflection maxima again coincide for minimum  $\Delta V$  (0.05 ml.). The volumetric accuracy is lower in this titration, but the same could be said of any electrometric system. An accuracy of 0.06 ml. is possible.

### Summary

A titrimeter is described for application to potentiometric titrimetry which is comparable in sensitivity to other electrometric methods.

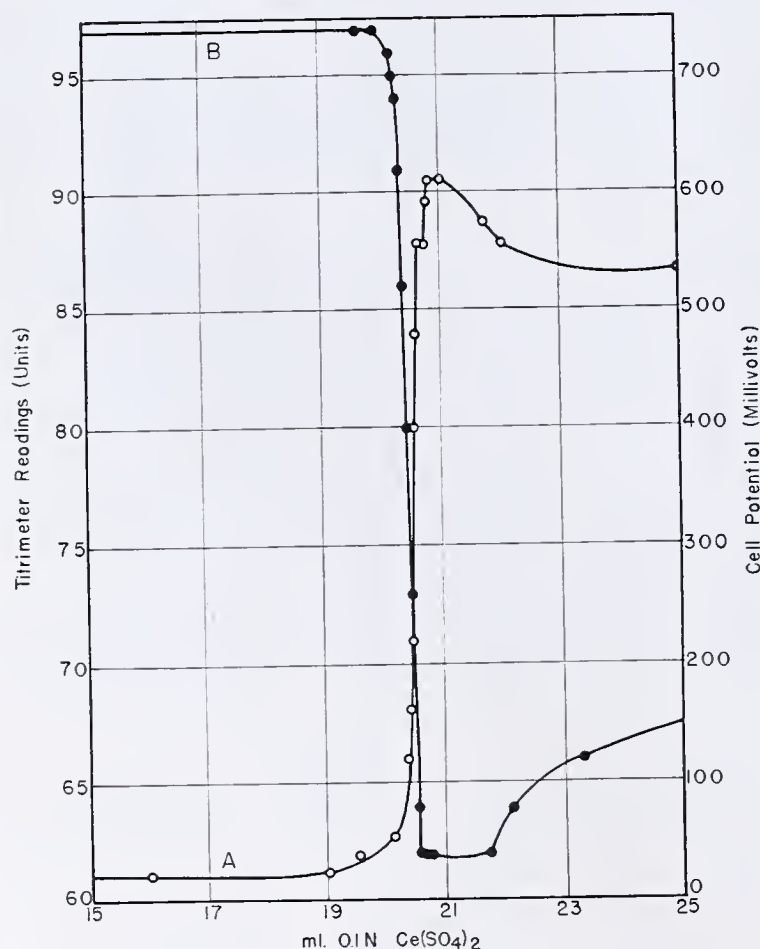


FIGURE 5. TITRATION OF 0.2 *N* FERROUS AMMONIUM SULFATE WITH 0.1 *N* CERIC SULFATE

A. Potential variations of cell *E* throughout reaction  
B. Titrimeter variations throughout reaction

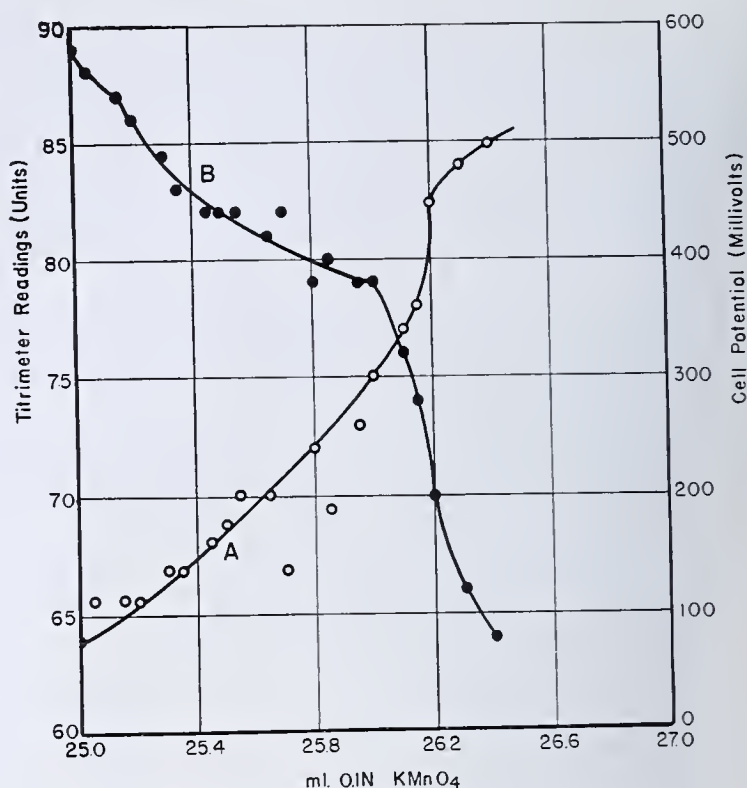


FIGURE 6. TITRATION OF TETRAVALENT VANADIUM (0.1 *N*) WITH POTASSIUM PERMANGANATE (0.1 *N*)

A. Potential variations of cell *E* throughout reaction  
B. Titrimeter variations throughout reaction

Its advantages over other electrometric systems may be summarized as follows:

1. Desensitizing polarization of the cell (*E*, Figure 1) is eliminated.
2. Maximum sensitivity is retained throughout the titration.
3. Inexpensive apparatus is used, which is readily obtainable.
4. Simplicity of operation; no adjustment is necessary for individual reactions.
5. There is positive and immediate indication of potential changes, which are roughly proportional to the actual potential variations of *E*.
6. Since the needle deflections are roughly proportional to the actual potential changes taking place in the cell, an inference can be made as to the potential variations taking place throughout any specific titration.
7. Reverse titration (back-titration) is easy and accurate.
8. Sensitivity is great enough for common electrometric titrations.
9. Adequate warning of the approach of the equivalence point is given.

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# Physical and Chemical Properties of Petroleum Fractions

## Handling Viscous Oils in Molecular Weight Studies

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An apparatus is described which permits exact and rapid introduction of accurately weighed quantities of viscous oil samples into a cryoscopic molecular weight apparatus by diluting the sample with a known quantity of solvent from the same source as used for the molecular weight apparatus. The molecular weights of several test oils have been determined. A comparison of these results indicates that the error caused by dilution will not exceed 2 per cent. Data obtained in the determinations of the molecular weights of three highly viscous samples are given.

and has been used successfully in handling viscous samples. In this apparatus the sample is dissolved in solvent from the same source as that employed for the cryoscope and its concentration accurately determined by weighing. The solution thus prepared is introduced into the molecular weight apparatus directly from the flask-pipet. The amount of solute added to and the increase in the amount of the solvent in the molecular weight apparatus can be calculated from the composition and weight of the increment added.

### Description and Operation of Flask-Pipet

Figure 1 shows the construction of the flask-pipet, which consists essentially of two major parts: (1) A flask, *B*, with a ground joint, *A*, inserted in the neck and, (2) fitting joint *A*, a cap equipped with pressure and delivery tubes. A quantity of oil,

**A** MOST useful and interesting property of a hydrocarbon is its molecular weight, and the determination of this property for petroleum hydrocarbons, which has been thoroughly reviewed by Headington (1), has been the object of considerable study by many investigators. The Bureau of Mines has studied the cryoscopic method of determining molecular weights in some detail and has published two papers (4, 5) on this subject. The present report concerns primarily a device that has been used successfully in the bureau's Petroleum Experiment Station laboratory at Bartlesville, Okla., for handling very viscous oils in cryoscopic molecular weight studies.

In determining the molecular weight of a liquid some type of weighing pipet is commonly used to weigh the sample and to introduce it into the molecular weight apparatus. A volumetric pipet with the tubes bent to prevent loss of liquid is usually satisfactory for reasonably fluid materials but is not suitable for liquids of very high viscosity. Such liquids have been handled in some laboratories (2, 3) by using thin-walled glass capsules, which are filled with the viscous sample and dropped into the molecular weight apparatus. This procedure seems more suitable for the ebullioscopic method than the cryoscopic. In the latter method serious loss of solution may attend removal of the capsule, dissolution of the oil from the capsule is more difficult owing to lower temperatures, and the capsule or its fragments if not removed may interfere with the stirring device, particularly the rotary type preferred by the writers.

The flask-pipet described in this paper eliminates the difficulties mentioned above

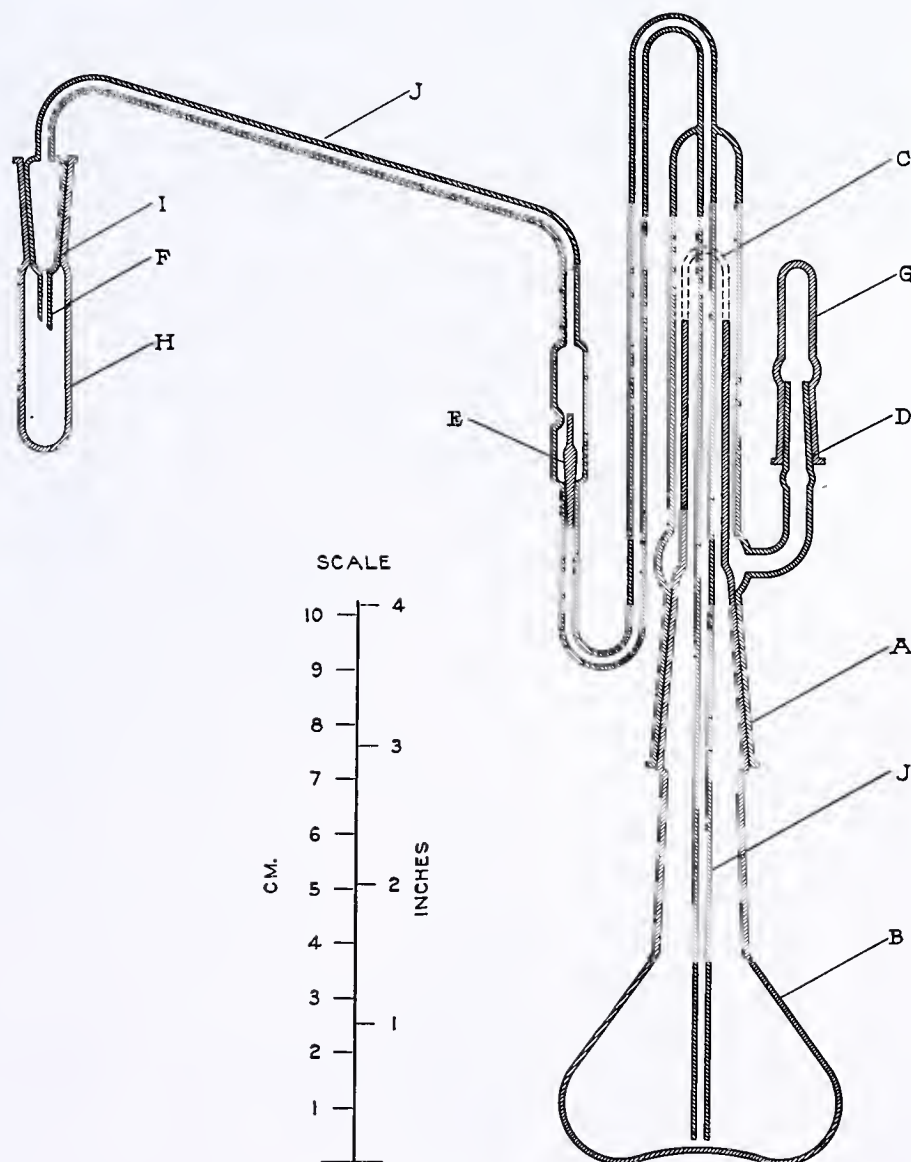


FIGURE 1



TABLE I. MOLECULAR WEIGHT DETERMINATION ON FOUR TEST OILS, DILUTED AND UNDILUTED PRIOR TO DETERMINATION

Sample No.	Diluent Added %	Molecular Weight of Oil	Error in Molecular Weight by Dilution Method %
0-8	None	669.5	
	30.79	677.9	+1.3
0-17	None	199.5	
	11.45	202.8	+1.7
0-18	None	719.9	
	38.37	729.3	+1.3
0-15	None	361.6	
	32.12	355.2	-1.8

TABLE II. PROPERTIES OF FOUR TEST OILS

No.	Sample Description	Refractive Index at 20.0° C.	Density at 20.0° C.	Viscosity at:			
				100° F. (37.8° C.)	130° F. (54.4° C.)	Kine-matic	Saybolt
				stokes	Universal <sup>a</sup>	stokes	Universal <sup>a</sup>
0-8	Acetone extract from Cabin Creek, W. Va., crude	1.4833	0.8768	2.367	1.094	1.019	471.7
0-17	Burning oil cut from Rodessa, La., crude	1.4472	0.8007	..	..	..	..
0-18	Commercial "bright stock" from mid-continent crude	1.5057	0.9094	10.05	4.643	3.334	1543
0-15	Shell sample 4, "light aromatic"	1.594 <sup>b</sup>	1.0346	..	..	8.87	4106

<sup>a</sup> Conversion by A. S. T. M. method D446-37T.<sup>b</sup> Too dark for accurate observation.

the molecular weight of which is to be ascertained, is introduced into flask *B* and its weight determined. Then sufficient solvent to make a fluid solution is added to the oil in the flask, which is again weighed after the neck is sealed at *C*. From these data the quantity of solvent and the concentration of the solute are determined.

The inside of the neck of the flask should be kept free of oil and solvent to prevent difficulties and loss of sample when the flask is sealed. Glass must not be lost in this operation, and the portion of the neck "sealed off" must be weighed with the flask. The flask should be shaken thoroughly to ensure the homogeneity of

its contents and left sealed until needed. To use this solution, tip *C* is cut off and the cap, carrying the delivery and pressure tubes, is quickly put in place as shown in the figure.

After the flask and auxiliary equipment are weighed, air pressure applied through the sidearm at joint *D* fills delivery line *J* with solution and forces it from pipet tip *F*. Valve *E* prevents return of liquid to the flask when pressure is removed, thereby avoiding bubbles in the delivery line that are troublesome when the next quantity of solution is expelled. Caps *G* and *H* prevent evaporation of the solvent. Joints *A* and *I* should be lubricated, but *D* is preferably left dry to avoid complications in weighing. Evaporation from this apparatus has been found to be negligible, as the average loss of weight was about 0.3 mg. in 16 hours. It is

obvious, however, that the apparatus must be protected from wide temperature variations to avoid loose joints and attendant "breathing" losses. If necessary, springs and glass hooks may be used to keep the joints tight. The particular apparatus described in this paper was constructed of ordinarily available glassware and weighed about 55 grams. An expert glassworker probably could make a lighter and more compact apparatus.

### Experimental Data

To ascertain the precision of this "method of dilution" the molecular weights of four petroleum oils were determined by the cryoscopic method (4), using both diluted and undiluted solutes. The solvent used was benzene,

dried with magnesium perchlorate. As shown in Table I and in Figure 2, the deviation in the extrapolated molecular weight due to using the "dilution" procedure is in each instance less than 2 per cent. Previous work has shown that this is well within the limits (4) within which two different laboratories would be expected to duplicate cryoscopic molecular weight determinations. It probably also approaches the limit of precision of an individual laboratory using conventional procedures. The points on the curves in Figure 2 were obtained

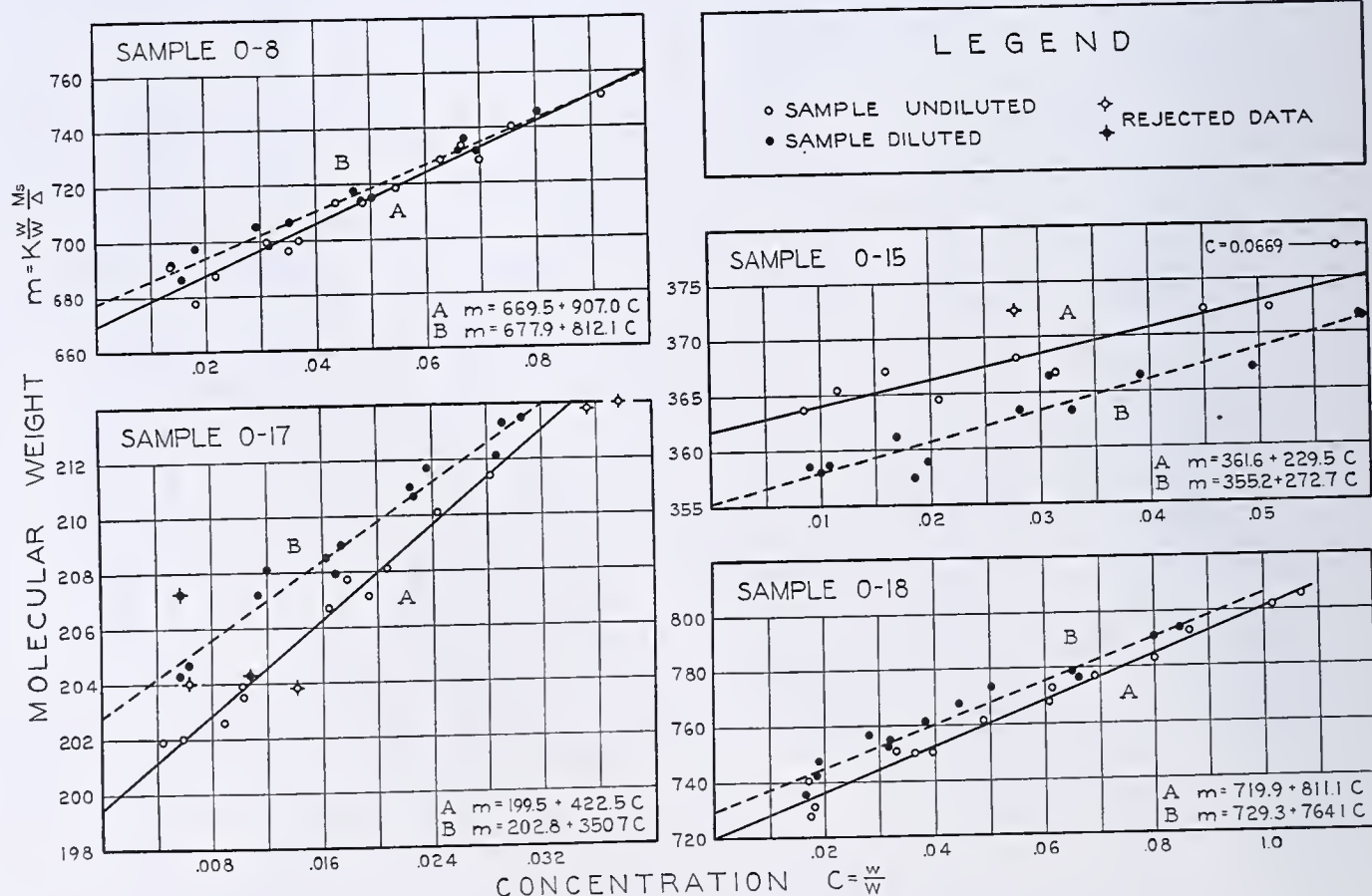


FIGURE 2



during the course of at least three separate series of two to six freezing-point determinations on each sample, and the equations given were derived by applying the method of least squares to the accepted data. A critical examination of the procedure and data did not disclose the reason for the small discrepancy between the two methods. Table II shows a few properties of the test samples and gives a brief description of their origin.

Table III and Figure 3 present the results of molecular weight determinations on three highly viscous samples, 0-19, 0-22, and 38. These had been diluted with benzene in the dispensing device described previously, giving oil concentrations of 65.32, 61.70, and 56.65 per cent, respectively. An

indication of the tacky nature of these samples is obtained from Table IV where a number of properties including viscosity are reported. The amount of solution prepared and the high molecular weight of sample 38, necessitating the use of

TABLE III. DATA OBTAINED IN DETERMINING MOLECULAR WEIGHTS OF SAMPLES 0-19, 0-22, AND 38

Sample	Run	Addition	Weight of Addition		
			Total Grams	Solute, w Grams	Solvent Grams
0-19	I	1	0.9745	0.6365	0.338
		2	2.0747	1.3552	0.720
		3	3.2144	2.0996	1.115
	II	4	4.4369	2.8982	1.539
		1	1.4080	0.9197	0.488
		2	2.5779	1.6839	0.894
	III	3	3.9989	2.6121	1.387
		4	5.0158	3.2763	1.740
		5	6.9284	4.5256	2.403
		1	0.8756	0.5719	0.304
		2	1.9929	1.3018	0.691
		3	3.7156	2.4270	1.289
0-22	I	1	1.5234	0.9399	0.584
		2	2.7896	1.7212	1.068
		3	4.1675	2.5713	1.596
	II	4	6.0580	3.7378	2.320
		1	1.3262	0.8183	0.508
		2	2.6017	1.6052	0.997
	III	3	4.0806	2.5177	1.563
		4	5.7570	3.5521	2.205
		5	6.9164	4.2674	2.649
	IV	1	1.3043	0.8048	0.500
		2	2.4830	1.5320	0.951
		3	4.2528	2.6240	1.629
38	I	4	6.0241	3.7169	2.307
		1	1.6643	1.0269	0.637
		2	3.0856	1.9038	1.182
	II	3	4.6803	2.8877	1.793
		4	6.0541	3.7354	2.319
		5	7.3487	4.5341	2.815
		1	3.2007	1.8132	1.388
		2	7.0133	3.9730	3.040
		3	10.7902	6.1126	4.678
		4	14.9911	8.4925	6.499
		1	4.1541	2.3533	1.801
		2	8.0899	4.5829	3.507
		3	11.8021	6.6859	5.116
		4	18.3275	10.3825	7.945

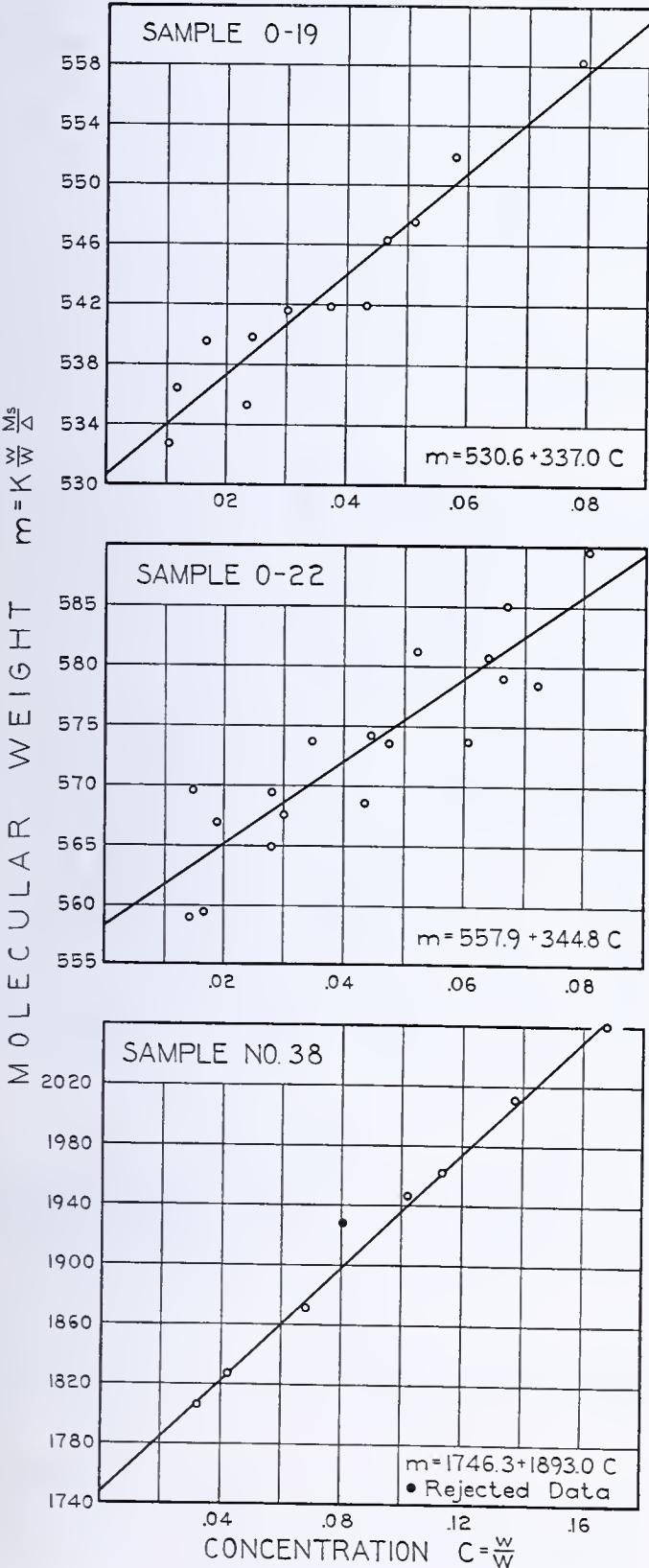


FIGURE 3

Sample	Weight of Solvent		Concn. w/W	Freezing-Point Depression °C.	m
	Original Grams	Total W Grams			
0-19	54.883	55.221	0.01153	0.110	536.4
		55.603	0.02437	0.231	539.8
		55.998	0.03749	0.354	541.9
		56.422	0.05137	0.480	547.6
		55.220	0.01666	0.158	539.5
	54.732	55.626	0.03027	0.286	541.6
		56.119	0.04655	0.436	546.3
		56.472	0.05802	0.538	551.9
		57.135	0.07921	0.726	558.3
		54.913	0.01041	0.100	532.7
	54.609	55.300	0.02354	0.225	535.3
		55.898	0.04342	0.410	541.9
		Extrapolated molecular weight			530.6
0-22	55.975	56.559	0.01662	0.152	559.4
		57.043	0.03017	0.272	567.6
		57.571	0.04466	0.398	574.2
		58.295	0.06412	0.565	580.7
		56.757	0.01442	0.132	558.9
	56.249	57.247	0.02804	0.254	564.9
		57.812	0.04355	0.392	568.5
		58.454	0.06077	0.542	573.7
		58.898	0.07245	0.641	578.4
		53.960	0.01492	0.134	569.6
	53.460	54.411	0.02816	0.253	569.4
		55.089	0.04763	0.425	573.5
		55.767	0.06665	0.589	579.0
		53.885	0.01906	0.172	566.9
		54.429	0.03498	0.312	573.7
38	55.062	55.041	0.05247	0.462	581.1
		55.567	0.06722	0.588	585.0
		56.063	0.08088	0.702	589.5
		Extrapolated molecular weight			557.9
	53.590	56.450	0.03212	0.091	1806.2
		58.102	0.06838	0.187	1871.1
		59.740	0.10232	0.269	1946.4
		61.561	0.13795	0.351	2011.1
		55.391	0.04249	0.119	1827.1
		57.097	0.08027	0.213	1928.4
		58.706	0.11389	0.297	1962.2
		61.535	0.16873	0.419	2060.6
		Extrapolated molecular weight			1746.3



TABLE IV. PROPERTIES OF HIGH-VISCOSITY OILS

No.	Sample Description	Refractive Index at 20.0° C.	Density at 20.0° C.	Viscosity at:			
				130° F. (54.4° C.) Kinematic stokes	Saybolt Universal <sup>a</sup>	210° F. (98.9° C.) Kinematic stokes	Saybolt Universal <sup>a</sup>
0-19	Shell sample 3, "heavy aromatic"	1.588 <sup>b</sup>	1.0225	..	..	3.184	1,481
0-22	Shell sample 3 BL	1.559 <sup>b</sup>	0.9976	50.05	23,170	1.661	773
38	Shell sample 5, polymerized isobutylene	1.5020	0.9015	..	..	103.4	48,000

<sup>a</sup> Conversion by A. S. T. M. method D446-37T.<sup>b</sup> Too dark for accurate observation.

large amounts of the solution in the determination, permitted only two runs to be made on this material. The separation or identification of the data for individual runs (Figure 3) is impossible for this sample as well as for the lower molecular weight samples 0-19 and 0-22 in which three and four runs, respectively, were made. Although the precision of the determination is better than 2 per cent there is no logical reason for believing that these samples behaved differently than did the four test oils. Consequently, if it can be assumed that the cryoscopic method used in this investigation gives correct molecular weights with undiluted samples, then the results obtained on the viscous oils may be considered as being accurate to  $\pm 2$  per cent.

## Acknowledgments

Of the seven samples used in this investigation four (0-15, 0-19, 0-22, and 38) were supplied by the Shell Development Company of Emeryville, Calif., and one (0-18) by the Mid-Continent Petroleum Corporation, Tulsa, Okla. The writers are grateful to S. Tijmstra and his co-workers of the Shell Development Company for their active interest and cooperation in problems relating to the molecular weights of petroleum fractions.

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# Determining the Amyl Alcohol Content of Distilled Spirits

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IN THE production of ethyl alcohol by fermentation there is produced a group of higher alcohols generically known as "fusel oils", which constitute an essential part of the congeners of alcoholic beverages. Although the fusel oil fraction is necessary for odor and taste characteristics, the amounts present are extremely small and range between 70 and 250 grams per 100 liters of distilled spirit.

Since the fusel oil fraction is used as a step in the assay analysis of distilled beverages, many tests have been developed for their quantitative determination. The preferred method of Allen-Marquardt, which is the official method and adopted as the standard by the Association of Official Agricultural Chemists, estimates the fusel oil content by extraction with carbon tetrachloride and subsequent oxidation to the respective acids, which are then quantitatively estimated by titration with standard 0.1 N sodium hydroxide. Modifications of this method have been described by Tolman and Hillyer (6) and Mitchell and Smith (6). Herzfeld and Rose (7, 9) describe a method by which the fusel oil is determined by a measure of the increase in the volume of chloroform used as the extractant.

Komarowsky (4) determined the fusel oils by means of a color reaction. Many authors (1, 3, 5, 10) have investigated the reactions responsible for the color produced by the combination of the alcohols of higher molecular weight with cyclic aldehydes such as salicylaldehyde, vanillin, veratric aldehyde, and *p*-dimethylaminobenzaldehyde. Penniman, Smith, and Lawshe (8) describe a method of analysis which appears to yield a true value for the fusel oil content of a distilled

spirit. However, their high values may be in error because during the treatment of the beverage with sulfuric acid and alkaline silver nitrate there is produced some acetic acid which reacts with the cyclic aldehydes and produces additional color (2).

In the present method, the fusel oil, separated from the distilled spirit by distillation and subsequent extraction with carbon tetrachloride, is determined by esterification with acetyl chloride (12). After the reaction is completed, the excess acetyl chloride is decomposed and titrated. The difference in titer between the sample and a blank gives the moles of acetic acid removed by esterification with the higher alcohols.

## Reagents

Eastman's reagent grade acetyl chloride is used in preparing a 0.23 M (molal) solution in dry toluene. The pyridine solution is made approximately 0.50 M in toluene. Both solutions may be kept safely in regular well-ground glass-stoppered bottles.

## Apparatus

The distillation unit recommended by the official Allen-Marquardt method is used to separate the fusel oil fraction and other volatile constituents from the solids of the whisky.

The reaction flask, shown in Figure 1, is made from a 125-ml. Erlenmeyer flask to which is attached a standard-taper ground joint No. 15. The neck of the flask is elongated as shown in order to assure no loss of reagents during pipetting.

In Figure 2 is shown the dehydration and dealcoholizing still used to remove the ethyl alcohol and water from the



composite carbon tetrachloride extracts. The still is packed with small glass helixes 0.64 cm. (0.125 inch) in diameter.

### Procedure

The sample of beverage to be analyzed (50 ml.) is placed in a 500-ml. Erlenmeyer flask equipped with a ground joint. Thirty milliliters of 0.1 *N* sodium hydroxide and a few pieces of silicon carbide (10-mesh) are added, and the flask is attached to the Allen-Marquardt distillation unit. When 45 ml. of distillate have been collected in a 125-ml. separatory funnel, the distillation is stopped and 25 ml. of distilled water are added to the residue. Distillation is then continued until the total volume of distillate is approximately 65 ml. To the distillate are now added 10 ml. of distilled water and 10 grams of sodium chloride and the contents are well shaken to dissolve most of the salt before beginning the extraction with carbon tetrachloride.

The extraction consists of four consecutive treatments with 40-, 30-, 20-, and 10-ml. portions of carbon tetrachloride, shaking at least 15 seconds upon each addition of carbon tetrachloride. The carbon tetrachloride extract is collected in the reaction flask (Figure 1) to which have been added a few pieces of silicon carbide to ensure even boiling. The reaction flask is attached to the still (Figure 2) and 50 ml. of distillate are collected by allowing the still to reflux for 5 minutes before removing the first fraction and then removing nine more consecutive fractions at 5-minute intervals. The reaction flask is allowed to cool 1 minute, removed while still warm, loosely stoppered, and cooled for from 3 to 5 minutes in an ice bath. To the flask are now added 5 ml. of pyridine solution and 10 ml. of acetyl chloride solution from precision pipets, being sure during the pipetting procedure that the respective reagents are introduced well down in the flask.

Immediately following the addition of the acetyl chloride solution the flask should be tightly stoppered. It is advisable to put a very small amount of lubricant on the stopper (just enough to make a seal but not enough to allow the stopper to blow out of the flask during the following heating period). The stoppered flask is then shaken and placed in a water bath (12) kept at 60° C. The flask is allowed to remain in the bath for 30 minutes with shaking every 5 minutes. It is then placed in an ice bath for 5 minutes, after which 25 ml. of water are added, washing down the neck of the flask during the addition. After the flask has been shaken to decompose all pyridine salts and to extract the acids into the aqueous layer, an excess (1 to 3 ml.) of 0.100 *N* sodium hydroxide is added from a buret, the flask is shaken vigorously, 4 or 5 drops of phenolphthalein are added, and the solution is back-titrated to a light pink with 0.100 *N* sulfuric acid.

A blank should be run with each set of experiments and the alcoholic hydroxyl groups in the sample estimated as the difference in alkali used between the sample and that of the blank. One milliliter of 0.1 *N* sodium hydroxide is equivalent to 0.0001 mole of fusel oil or 0.0088 gram of fusel oil or 17.6 grams of fusel oil per 100,000, calculated as amyl alcohol.

The accuracy of the method was tested by using a carbon tetrachloride solution containing a known amount of *sec*-butylcarbinol. The latter had a refractive index at 25° C. of 1.4084 and boiled between 129.35° and 129.55° C. In all experiments the results indicated a recovery of approximately 96 per cent, which may be assumed to be quantitative, since the alcohol used had a boiling range of 0.2° C. and undoubtedly contained a small percentage of inert substance.

Because of the small concentrations of amyl alcohol used, it was found necessary to heat the reaction mixture at least 30 minutes during esterification. In Table I are given the results obtained by heating for 20 and 30 minutes, respectively.

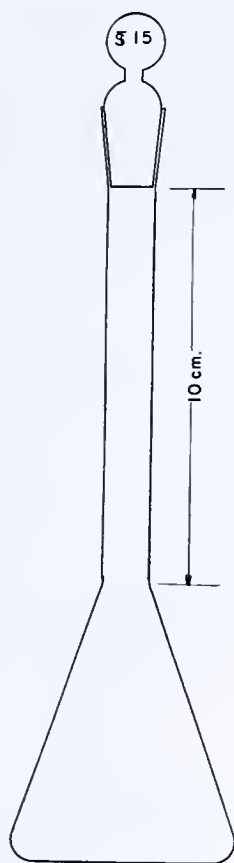


FIGURE 1

Heating for longer than 30 minutes is apparently not necessary. In one experiment *sec*-butylcarbinol was extracted from an ethyl alcohol solution with carbon tetrachloride and subsequently freed from ethyl alcohol and water by distillation prior to the esterification process. One set of samples was heated for 30 minutes and another set for 40 minutes, yet the same number of moles of alcohol were recovered.

TABLE I. EFFECT OF HEATING

Time of Heating Min.	Alcohol Present Mole	Alcohol Found Mole
20	0.000474	0.000396
30	0.000474	0.000456

According to Smith and Bryant (12) the presence of aldehydes or esters does not interfere with the determination. In Table II are given the results obtained when equal molal quantities of acetaldehyde and ethyl acetate dissolved in carbon tetrachloride were added to the carbon tetrachloride solution of *sec*-butylcarbinol prior to the determination.

TABLE II. EFFECT OF ALDEHYDES AND ESTERS

<i>Sec</i> -Butylcarbinol Mole	Ethyl Acetate Mole	Acetaldehyde Mole	Alcohol Found Mole
0.00047	0	0	0.000410
0.00047	0.00065	0	0.000415
0.00047	0	Approx. 0.001	0.000420

Further confirmation, presumably, of the negative effect of esters was obtained by determining the fusel oil content of a whisky by distilling immediately upon the addition of alkali, and by refluxing the whisky for 0.5 hour with alkali prior to distillation. The results are given in Table III and indicate either that complete saponification had occurred during the distillation process, or that esters do not interfere with the test.

Although the results obtained on solutions of *sec*-butylcarbinol in carbon tetrachloride were practically quantitative (96 per cent), it became evident that the results obtained on *sec*-butylcarbinol in 100-proof ethyl alcohol showed a recovery of only approximately 83 per cent. By experiment it was shown that the loss occurred in the extraction process, and the magnitude of the loss was proportional to the volume of solution (ethyl alcohol-water) containing the *sec*-butylcarbinol.

In one set of experiments, 50 ml. of 100-proof alcohol containing *sec*-butylcarbinol were distilled with 50 ml. of satu-

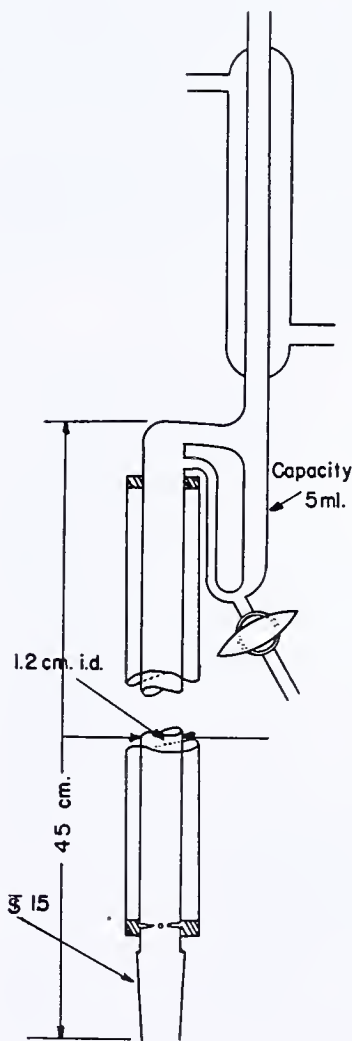


FIGURE 2. DISTILLATION UNIT



rated salt and then extracted, while in another set 50 ml. of 100-proof ethyl alcohol containing *sec*-butylcarbinol were diluted with 110 ml. of saturated salt solution. The moles of alcohol recovered were 0.000459 and 0.000411, respectively, which indicates a loss of approximately 10 per cent of *sec*-butyl alcohol in the solution having the greater volume.

TABLE III. EFFECT OF REFLUXING

Treatment Prior to Distillation	Alcohols Esterified Mole
Distilled immediately	0.00102
Reflux 0.5 hour prior to distillation	0.00102

Accordingly, the method for the initial distillation of the whisky was modified to yield a small volume of distillate which would be sure to contain all of the fusel oil fraction. In Table IV are given the results obtained, which indicate that all of the fusel oil fraction was recovered by the modified method of distillation and that the loss in fusel oil presumably occurs in the extraction process.

### Comparison of A. O. A. C. and Acetyl Chloride Methods

The acetyl chloride-pyridine method of analysis offers considerable advantage over the official A. O. A. C. method. The time required for a complete analysis by the acetyl chloride method is approximately 3 hours by virtue of the elimination of the lengthy oxidation procedure. The method is not affected by aldehydes, which if present in the whisky must be removed prior to the analysis according to the official method. Since esters do not affect the results, saponification prior to the initial distillation is not necessary. By obtaining only 65 ml. of distillate instead of 110 ml., the time required for the initial distillation is almost halved. Further, it is not necessary to saturate the distillate to a definite salt concentration, since an excess of salt does not affect the results of the new method. Errors in the regular extraction procedure are reduced, since after the initial extraction of the alcohols with carbon tetrachloride, the present procedure removes traces of water and ethyl alcohol by simple distillation rather than by subsequent extraction with saturated sodium chloride solution followed by extraction with saturated sodium sulfate solution.

TABLE IV. EFFECT OF MODIFIED METHOD

(Mixture of <i>sec</i> -butylcarbinol in 100-proof ethyl alcohol)		
Treatment of Sample	Alcohol Present Mole	Alcohol Recovered Mole
Modified distillation and extraction	0.00046	0.000377
No distillation, only extraction	0.00046	0.000380

During the distillation procedure used for the dehydration and dealcoholization of the carbon tetrachloride extract, the ternary azeotrope ethyl alcohol, water, and carbon tetrachloride are removed first. Dry ethyl alcohol remaining after the water has been removed then forms a binary azeotrope with carbon tetrachloride which has a boiling point approximately 11.5° C. below that of carbon tetrachloride itself, and is readily removed. It is fortunate that carbon tetrachloride does not form any azeotropes with alcohols boiling above *n*-butyl alcohol by virtue of the wide difference in boiling points between carbon tetrachloride and the higher alcohols.

The azeotropic power as exhibited by carbon tetrachloride with alcohols is conducive to a simple distillation procedure for the removal of extraneous amounts of ethyl alcohol and water. The method allows for a complete removal of the lower alcohols, since distillation can proceed long after the ethyl alcohol has been removed, by distilling only carbon tetrachloride, without fear of the loss of any of the higher alcohols.

The presence of isopropyl, *n*-propyl, *tert*-butyl, and iso-butyl alcohols and their removal during the distillation procedure would indicate a decrease in value for fusel oils. It may be assumed that a similar decrease in fusel oil value is obtained by the official method, since the percentage amounts of alcohols lower than the amyls present in fusel oil are small, and, too, that since the solubility of the low boiling alcohols is more closely related to the solubility of ethyl alcohol than the amyls, the extraction of the carbon tetrachloride extract with saturated sodium chloride and sodium sulfate solution would remove a considerable portion.

After removal of the water and alcohol from the carbon tetrachloride extract, the fusel oils present require only 30 minutes for complete esterification; whereas an oxidation procedure requires at least 8 hours, plus a subsequent distillation. The subsequent titration of the excess acetyl chloride is analogous to that of the official method, using 0.1 *N* sodium hydroxide as titer and phenolphthalein as indicator. However, since the results depend on the determination by difference between the amount of acetyl chloride added and the amount remaining after esterification, it is necessary to know accurately the amount of acetyl chloride added.

TABLE V. COMPARISON OF METHODS

Treatment	Allen-Marquardt	Acetyl Chloride
Residue	0.000355	0.00035
Distillate	0.000049	.....
Not distilled	0.000395	.....

In Table V is given a comparison of the results obtained by the two methods using a standard sample of *sec*-butylcarbinol in solution in 50 per cent ethyl alcohol. The samples of *sec*-butylcarbinol in 50 per cent ethyl alcohol were subjected to the following procedure prior to the oxidation and esterification reactions.

Fifty milliliters of *sec*-butylcarbinol solution were diluted with saturated salt solution and sodium chloride to a density of 1.1. This was then extracted with 40-, 30-, 20-, and 10-ml. portions of carbon tetrachloride and the extract washed three and two times with saturated sodium chloride and sodium sulfate solutions, respectively. The solutions were then subjected to distillation in the dehydration stills and 50 ml. distilled off as distillate. Because of the large excess of water present, the acetyl chloride method could not be applied successfully to determine the amounts of alcohols contained in the distillates.

However, the usual method of procedure as outlined in the Allen-Marquardt method allows a considerable amount of ethyl alcohol to remain in the carbon tetrachloride extract, which in the usual procedure attributes considerably to the final evaluation of fusel oil content.

TABLE VI. COMPARISON OF METHODS

Treatment	Allen-Marquardt	Acetyl Chloride
Residue	0.000997	0.00096
Distillate	0.000200	0.00045
Not distilled	0.001180	0.00145

In another experiment using a standard sample of whisky, it was again evident that results obtained by the Allen-Marquardt method are too high, owing to the existence of some ethyl alcohol in the carbon tetrachloride extract. The results of the experiments are given in Table VI. The samples were subjected to the same treatment prior to distillation as the *sec*-butylcarbinol solution, except that the esters in the whisky were destroyed by the usual method subsequent to the distillation to remove extraneous solid or nondistillable material from the fusel oil fraction.

It is again evident that considerable amounts of ethyl alcohol are present in the carbon tetrachloride extract and con-



tribute to the value of fusel oil as normally determined. However, the acetyl chloride method indicates the presence of considerably more alcoholic hydroxyl groups than the Allen-Marquardt method. The major portion of the difference lies in the distillate, and indicates that the oxidation procedure is not capable of oxidizing quantitatively ethyl alcohol to the corresponding acid. This fact was corroborated by another set of experiments in which carbon tetrachloride containing a small amount of ethyl alcohol was subjected to both procedures. By the Allen-Marquardt method 0.00074 mole of alcohol was recovered; by the acetyl chloride method, 0.000975 mole. This is in agreement with the conclusions of Schidrowitz and Kaye (11), who indicated that ethyl alcohol was not oxidized quantitatively during the oxidation procedure.

In the Allen-Marquardt method a blank must be run to determine the acidity produced by the carbon tetrachloride in the oxidation procedure.

TABLE VII. GENERATION OF ACIDS

CCl <sub>4</sub> Used Ml.	Acid Found Mole
25	0.000020
50	0.000025
100	0.000020

Several experiments were made to determine the true cause of the generation of acids during the oxidation procedure. The results, given in Table VII, indicate that the acids are not generated by virtue of impurities in the carbon tetrachloride but by the partial decomposition of the carbon tetrachloride itself.

It is evident that the evaluation of fusel oil in distilled spirits

depends upon the method used for the determination. Each method produces accurate values which are relative, but not in agreement when compared with values obtained by different procedures. Each procedure, used previously, is not specific for alcoholic hydroxyl groups alone, but is affected by the presence of other reactive groupings such as aldehydes, unsaturates, and esters. The acetyl chloride esterification procedure is normally not affected by the presence of these groupings and tends to give values which are specific for hydroxyl groups.

However, according to the method as outlined for the acetyl procedure, any alcohol below *n*-butyl will be excluded from the fusel oil value. In view of these considerations, the results obtained by the acetyl chloride method are designated as an "amyl alcohol" value and not as a "fusel oil" value.

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## Kniasseff Fat Test

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FOR twelve years the writers have made comparative analyses of ice creams and ice milks, taking the methods of Mojonier and the Association of Official Agricultural Chemists as standard, and attempting to correlate the results of some twenty-five modifications of the Babcock method with the standard results. With only one method has it been possible to obtain even approximate results consistently in a series of comparisons when a suitably wide range (4 to 20 per cent) of fat content has been employed.

The exceptional method is that of Kniasseff (2), which, in the authors' hands, has yielded results of a high order of accuracy when suitable corrections have been applied. The method is lengthy, however, and the advantage of speed which Babcock-type methods inherently possess over the solvent-extraction methods is lost, if but one or two estimations are to be made.

The purpose of this note is to outline minor changes in the Kniasseff procedure which appear to increase the accuracy and the speed attainable.

### Reagents and Procedure

REAGENT I. Distilled water, 1000 ml.; sodium hydroxide, A. C. S., 132 grams; ammonium sulfate, A. C. S., 42.8 grams.

REAGENT II. Ethyl alcohol, U. S. P., 391 ml.; *n*-butyl alcohol, b. p. 116–118° C., 24 ml.; ammonium hydroxide,

A. C. S., 24 ml.; ethyl ether, A. C. S., 94 ml.; petroleum ether, b. p. 26–31° C., 94 ml.

PROCEDURE. 1. Weigh  $9 \pm 0.02$ -gram duplicate samples into 9-inch, 9-gram, 50 per cent Babcock cream test bottles which have been proved accurate by mercury calibration. The writers discarded bottles with errors greater than 0.1 per cent in the ranges 50 to 40 per cent, 50 to 30 per cent, and 50 to 20 per cent.

2. Add  $8 \pm 0.1$  ml. of reagent I. Shake 5 seconds with rotary movement.

3. Add  $5 \pm 0.1$  ml. of reagent II. Shake 10 seconds.

4. Digest 5 minutes at  $84 \pm 1^\circ$  C., shaking 5 seconds after 1.5, 3.5, and 5 minutes. If foam rises above 40 per cent mark, remove bottle for an instant, then reimmerge.

5. Centrifuge  $30 \pm 5$  seconds at relative centrifugal force of  $165 \times$  gravity at base of bottle at  $65 \pm 5^\circ$  C.

6. Add tap water at  $70 \pm 5^\circ$  C. to base of neck. Do not agitate.

7. Centrifuge  $30 \pm 5$  seconds as before.

8. Add water to 50 per cent mark.

9. Centrifuge  $60 \pm 5$  seconds.

10. Place in water bath at  $60 \pm 2^\circ$  C., so adjusted that temperature falls to  $57^\circ$  C. in 10 to 20 minutes.

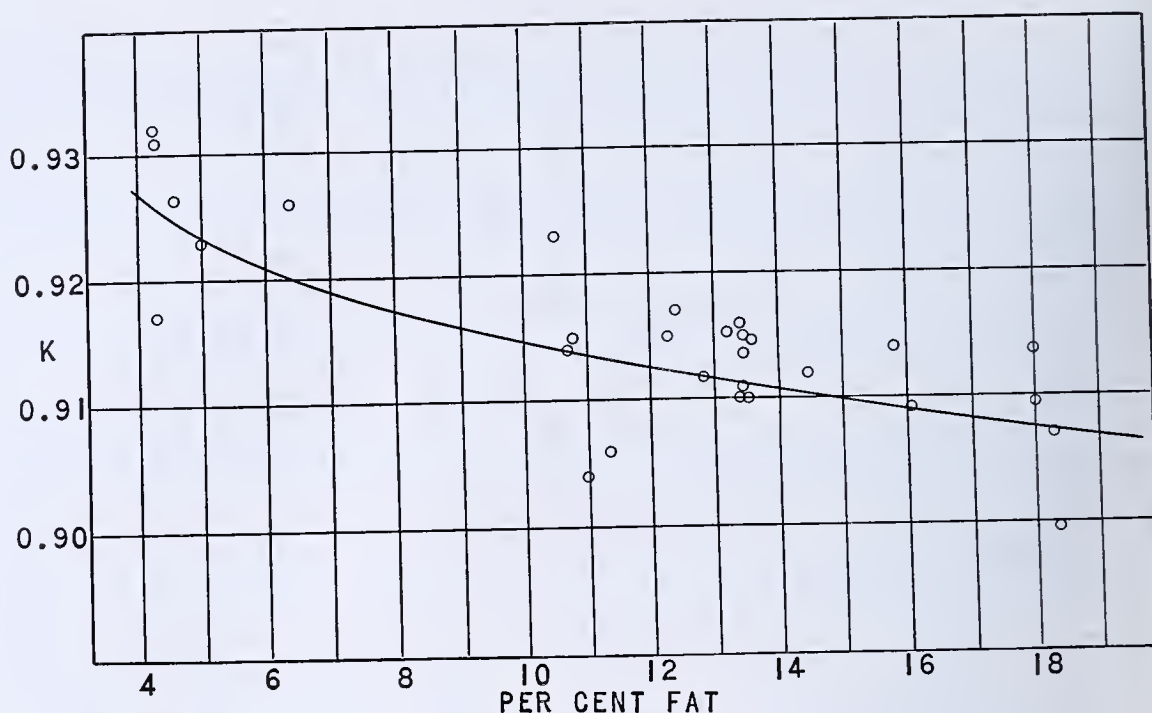
11. When temperature reaches  $57 \pm 0.5^\circ$  C., add oil and read.

12. Multiply reading by appropriate factor, *K*, obtained from Figure 1.

I. CHANGES IN KNIASEFF PROCEDURE. Reagent II undergoes some change in composition due possibly to amine forma-



FIGURE 1



tion. It is recommended, therefore, that the solution age one week before being used.

II. It is recommended that reagent II be stored under screw caps with liners of metal foil instead of under ground-glass stoppers. The ordinary ground-glass closure permits the low-boiling fractions to evaporate.

III. As originally devised, the method required a digestion period of 15 minutes. In the present work a 5-minute period has proved to be sufficient.

IV. Completed tests should be read from a water bath the temperature of which is falling, in order that the menisci may have constant volumes.

V. The results should be multiplied by a factor which is a function of the fat content.

Figure 1 was derived as follows:

Thirty mixtures, varying in size from 1000 to 15,500 pounds, were prepared under commercial conditions, pasteurized, homogenized, cooled, and thoroughly mixed. One sample was taken from each batch and was analyzed for fat by one of the authors, using the Mojonnier method. At the same time, the other worker estimated the fat content of the same sample, using the modified Kniaseff procedure. The fat contents varied from 4.2 to 18.3 per cent (Kniaseff). The mean Kniaseff result was multiplied by the factor necessary to equal the Mojonnier in each case and the factors found were laid out as circles on the graph. The smooth curve which would yield the minimum variation in the extreme cases was then drawn. This seemed wiser than the usual statistical procedure, for the number of observations was much too small to justify least squares treatment. No analyses were suppressed or discarded.

### Discussion

A large number of comparisons have been made, using frozen products of several flavors, with apparently the same order of accuracy, but the results are not tabulated because frozen samples cannot be prepared and analyzed invariably with the accuracy requisite to a comparison of this nature. This is well known and has been reported by many, notably by Bird and Johnson (1). In the writers' experience duplicate Mojonniers on mixes have differed no more than 0.05 per cent, while carefully sampled frozen products have shown differences between duplicates as great as 0.26 per cent.

Because the Kniaseff method is empirical, balancing fat losses from hydrolysis and saponification with gains from dissolved solutes, the physical treatment accorded the sample is of the utmost importance. For this reason, all variables were controlled as closely as was practicable. However, it appears that operations 2 and 3 can be performed more roughly (3). Also, operation 5 is probably satisfactorily done at a relative centrifugal force of 100 to 200  $\times$  gravity, for the density differential between the fat and the surrounding liquid is large (0.82/1.02 at 60° C., at end of test).

The data pertinent to this paper are presented in Table I. Columns 1, 2, and 3 give the Kniaseff results, column 4 gives

the circle values of Figure 1, the fifth column contains the  $K$  values represented by the curve, the sixth column represents the "corrected" Kniaseff results—i. e., column 3 values multiplied by those of column 5—and the last column gives variations of the Kniaseff results from the Mojonniers.

TABLE I. KNIASEFF AND MOJONNIER RESULTS

Kniaseff I	Kniaseff II	Mean	$K$ Actual	$K$ Curve	Corrected	Mojonnier	Difference
4.10	4.30	4.20	0.932	0.927	3.89	3.91	-0.02
4.20	4.30	4.25	0.931	0.927	3.94	3.96	-0.02
4.90	5.00	4.95	0.923	0.923	4.57	4.57	...
4.20	4.25	4.22	0.917	0.927	3.91	3.87	-0.04
4.40	4.80	4.60	0.927	0.924	4.25	4.26	-0.01
6.30	6.40	6.35	0.926	0.920	5.84	5.88	-0.04
10.35	10.55	10.45	0.923	0.913	9.54	9.64	-0.10
10.60	10.70	10.65	0.913	0.913	9.72	9.72	...
10.75	10.75	10.75	0.915	0.913	9.81	9.84	-0.03
10.90	11.00	10.95	0.903	0.913	10.00	9.89	+0.11
11.20	11.40	11.30	0.906	0.913	10.32	10.24	+0.08
12.20	12.30	12.25	0.915	0.912	11.17	11.21	-0.04
12.35	12.35	12.35	0.917	0.912	11.26	11.32	-0.06
12.80	12.80	12.80	0.912	0.912	11.67	11.67	...
13.15	13.25	13.20	0.916	0.912	12.04	12.09	-0.05
13.30	13.40	13.35	0.917	0.912	12.18	12.24	-0.06
13.40	13.40	13.40	0.915	0.912	12.22	12.26	-0.04
13.50	13.70	13.60	0.915	0.912	12.40	12.44	-0.04
13.40	13.50	13.45	0.914	0.912	12.27	12.29	-0.02
13.30	13.60	13.45	0.911	0.912	12.27	12.25	+0.02
13.30	13.50	13.40	0.910	0.912	12.22	12.19	+0.03
13.50	13.50	13.50	0.910	0.912	12.31	12.29	+0.02
14.40	14.50	14.45	0.912	0.911	13.16	13.18	-0.02
15.80	15.80	15.80	0.914	0.909	14.36	14.44	-0.08
16.10	16.10	16.10	0.909	0.909	14.63	14.63	...
16.00	16.20	16.10	0.909	0.909	14.63	14.63	...
17.80	18.10	17.95	0.913	0.907	16.28	16.39	-0.11
18.00	18.00	18.00	0.909	0.907	16.33	16.36	-0.03
18.25	18.25	18.25	0.907	0.907	16.55	16.55	...
18.15	18.45	18.30	0.899	0.907	16.60	16.45	+0.15

Although these results indicate that 90 per cent of the corrected Kniaseff tests agree within 0.1 per cent of the Mojonnier values and that no variation exceeds 0.15 per cent, the fact that Kniaseff duplicates differed by as much as 0.4 per cent indicates that this excellent state of affairs is partly adventitious. A larger series would doubtless prove the point.

In conclusion, it is suggested that any individual Kniaseff fat test, run as outlined above, will probably be within 0.4 per cent of the truth and that the mean of duplicates will be within 0.25 per cent.

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# An Electrodialyzer for Starch

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THE apparatus described in this article was developed for the electrodialysis of starch and starch products. The process was used to remove all ions and at the same time to cause a coagulation of portions of the carbohydrate material which would facilitate its recovery.

Various forms of apparatus have been used for electrodialysis. The apparatus of Taylor and Kerecztsey (4) was unsatisfactory because the electrodes were too small and too far apart. The Löddesöl (2) modification of Pauli's (3) apparatus was better suited for this purpose because it was a three-chambered apparatus used in a horizontal position, with the electrodes fairly close together. Other dialyzers described in the literature either handle very small volumes or, if of large capacity, use electrodes other than platinum in hard-rubber containers to reduce costs of construction.

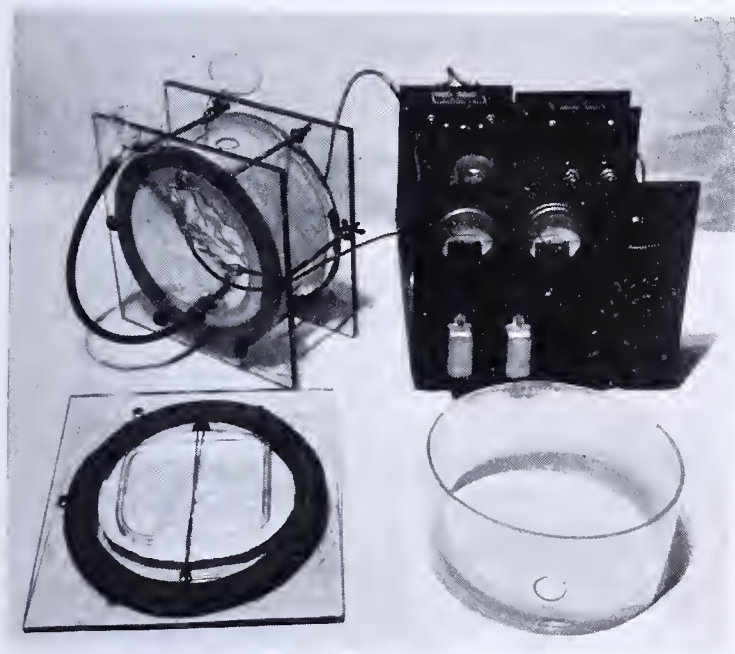


FIGURE 1. ELECTRODIALYZER

An electrodialyzer for quantitative work on starch should meet the following requirements:

1. Since the concentration of starch used cannot be much greater than 1 per cent, the dialyzate compartment should have a high capacity.
2. Since the conductance of starch pastes is very low, the electrode area must be large to give high current capacity.
3. To avoid excessive costs of platinum, the anode must be designed to use thin foil. Graphite or base metals cannot be used for quantitative work.
4. The volume of the electrode compartments should be small for convenient recovery of the small amounts of electrolytes removed from the starch.
5. The dialyzer must be easily dismantled for cleaning and removal of the coagulated starch paste.

The apparatus described below is a modification of the Löddesöl cell to meet these requirements.

Figure 1 is a photograph of the completely assembled apparatus; it also shows an extra center chamber, the construction of one end plate, and the vacuum-tube rectifier used as a source of current.

The center cell was constructed of a glass cylinder of about 1500-cc. capacity with parchment membranes stretched over the ends. The whole was clamped between the two end plates 20 cm. (8 inches) square, by means of 10-cm. (4-inch) bolts, with rubber gaskets 3 mm. (0.125 inch) thick serving as spacers between the parchment and the glass plates. The capacity of the electrode compartments thus formed was almost 75 cc. The electrodes were held in place against the glass plates as shown in Figure 1 by rectangles of glass tubing and rubber bands. The glass rectangles also served the purpose of supporting the parchment membranes.

The positive electrode was an oval (14.38 × 16.25 × 0.0025 cm., 5.75 × 6.5 × 0.001 inch) of platinum foil and the negative electrode was an oval of copper foil as recommended by Humfield and Alben (1). Electrical connections were secured by short wires leading through holes in the top of the glass plates and held in place beneath the foil by the rubber band arrangement.

The outlets to the electrode chambers were short glass tubes through stoppers in holes in the plates. Rubber tubes carrying small funnels were connected to these outlets in order to facilitate draining and refilling the electrode chambers. The apparatus was cooled by allowing cold water to flow over the sides when the whole cell was supported over a pneumatic trough.

Any source of direct current electricity can be used with this type of apparatus. In the electrodialysis of carbohydrates it was convenient to use a vacuum-tube rectifier with either resistance or transformer steps in order to vary the voltage applied. Variation in the current source from 0 to 500 volts with a capacity of 100 milliamperes is necessary.

The progress of the electrodialysis was followed by noting the voltage and current going through the cell, and also by titrating the liquid from the electrode chambers with 0.1 N acid or base. With starch products the cations were removed most rapidly, as noted by Watson (5).

TABLE I. RATE OF DIALYSIS OF 1 PER CENT CORNSTARCH PASTE

Time Hours	Amperage Milliamps. <sup>a</sup>	Rate of Electrolyte Removal, 0.1 N Acid or Base	
		Anode Cc./hour	Cathode
0	150		
0.5	105	5.2	9.4
1.0	85	4.2	1.5
2.0	65	3.2	0.9
3.0	55	2.3	0.7
4.0	40	1.9	0.6
5.0	30	1.6	0.6
6.0	28	1.3	0.5
7.0	28 <sup>b</sup>	1.1	0.4
11.0	28 <sup>c</sup>	0.6	0.3
15.0	28 <sup>d</sup>	0.3	0.1

<sup>a</sup> To get comparative readings, current source was adjusted to 200 volts before each reading.

<sup>b</sup> Free electrolyte practically all removed.

<sup>c</sup> Distinct separation of gel phase is apparent.

<sup>d</sup> Separation of gel phase is complete.

The data presented in Table I are characteristic of the operation of the electrodialyzer on a 1 per cent cornstarch paste. The applied voltage was increased from 200 at the beginning of dialysis to 500 volts in the course of 4 or 5 hours, taking care that the current was never more than about 100 milliamperes.

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# A Greaseless High-Vacuum Valve

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IN THE investigation of gases, particularly in the field of reaction kinetics, the impurities introduced with the stopcock lubricant have caused a great deal of difficulty. In order to work with chlorine systems where a small amount of foreign gas may completely change the kinetics, Bodenstein (1) constructed an all-glass valve that has been used with success. Ramsperger (2) designed a valve making use of a metal diaphragm with silver chloride as the seating surface. The authors have designed a more rugged and compact valve, also using silver chloride as the seating surface.

The details of construction are given in Figure 1. A silver seat, *B*, covered with silver chloride and mounted on a metal diaphragm is pressed against the polished end of the glass valve stem at *A*.

The glass parts of the valve are of Pyrex. The diaphragm is a platinum alloy, covered with a thin layer of silver chloride, and sealed to the outer edge of the glass by silver chloride. The glass is platinized to give a metallic surface over which the molten chloride will flow. It was found that a properly fitted diaphragm rim accomplished the same purpose, the contraction of both metal and chloride on cooling giving a very satisfactory seal.

The valve seat, *B*, is of silver with silver chloride on the inside, well compacted and shaped to fit *A*. The internal diameter of *A* is around 3 mm., thus permitting rapid flow of gas. The entire surface of *B* is covered with the chloride. The silver part, *C*, extends through the diaphragm and is screwed into *B*. The gas seal between *B* and the diaphragm is by means of silver chloride. The brass piston, *D*, is screwed tight to *C* and is thrust downward by the spring, which has a pressure of less than 40 kg. (80 pounds) per square mm. of bearing surface on *A*, as it was found that the silver chloride would flow if the pressure were much greater. A lug through the outer brass case prevents twisting. The vertical motion is controlled by the thumbscrew, *E*, and is limited by the stop on the cap, *F*, to between 0.5 and 1.0 mm.

When the valve is assembled the final seating is made by supporting the valve rigidly under the lower end, turning the thumbscrew to "close" until it is free, and putting a steel ball in the top of cap *F*. The ball is tapped lightly several times with a small hammer, 30 grams (1 ounce). The piston is raised and lowered, and the tapping is repeated. This is done several times. The extent to which the silver chloride has been compacted can be observed by the change in the position at which the thumbscrew just engages in lifting the piston. The chloride layer is about 0.5 mm. thick. If re-seating is necessary the same procedure can be used.

When the valves are in the apparatus the high-tension coil cannot be used for detecting leaks because of injury to the silver chloride surface. It is best to assemble the glass parts without the valves, test as usual, and then put in the valves. Leaks from the last operation can be detected by some technique such as the use of the Apiezon clay-oil product. It is important to prevent solid particles, particularly glass, from being blown through the valve. If glass is to be cut, the inside pressure should be brought to one atmosphere.

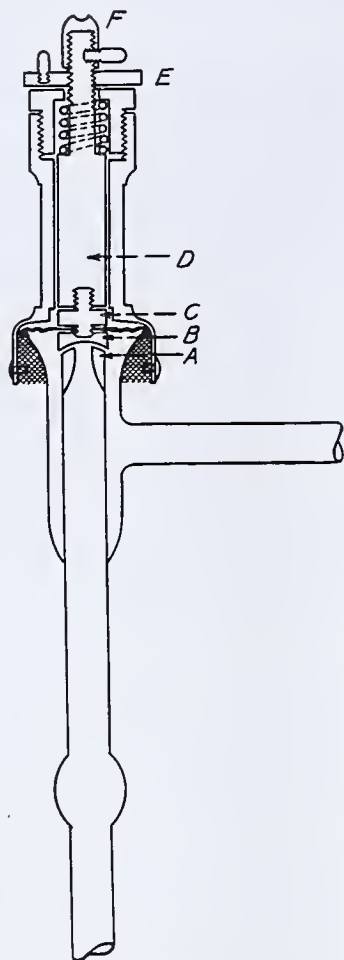


FIGURE 1

A considerable number of these valves have been made and tested by observing the leak through the seat as measured on a McLeod gage of 300-cc. capacity. This leak was generally less than 0.0001 mm. per hour. No measurable leak that could be attributed to the outer diaphragm glass seal was observed. There was no effect of seating the valve with or without an atmosphere differential on the diaphragm. The valve pumps out quickly, there being no outgassing as is usually experienced with ordinary greased stopcocks. The layer of silver chloride on the metal parts prevents gas from coming from this source.

It seems probable that the valve would be serviceable at higher temperatures. The upper limit would be the temperature at which silver chloride would flow under the pressure necessary for closure.

## Acknowledgment

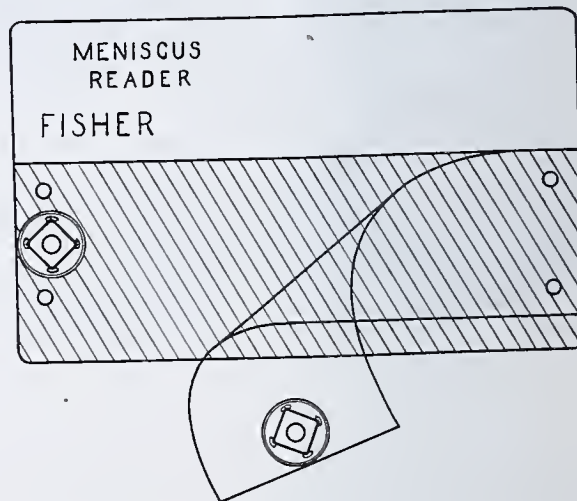
The authors wish to acknowledge their indebtedness to the Klett Manufacturing Company for the construction of this valve and for many useful ideas in its design.

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## Improvement for a Meniscus Reader

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FOR those doing numerous titrations and using a meniscus reader, the ease of reading the meniscus is offset by the need of removing the buret from its holder each time to slide the reader from the top to the bottom reading. This operation can be eliminated by making a slight change in the reader as shown in the diagram.

The tubular rivets holding one side of the reader together are removed to free the clear celluloid from the black and white. The top rivet is replaced to hold the black and white celluloid together. One part of an ordinary snap fastener is placed on the clear celluloid and the other part is placed on the black. This may be done by making small holes in the celluloid and tying the fastener on with a heavy thread. The fastener is placed near the edge of the reader, so that a fingernail can be inserted to pry it open. The meniscus reader can then be easily snapped on and off the buret.

This improvement makes it possible for the meniscus reader to be used on gas burets as easily as on any other type.



# Solenoid Stirring Device for Use in Confined Spaces

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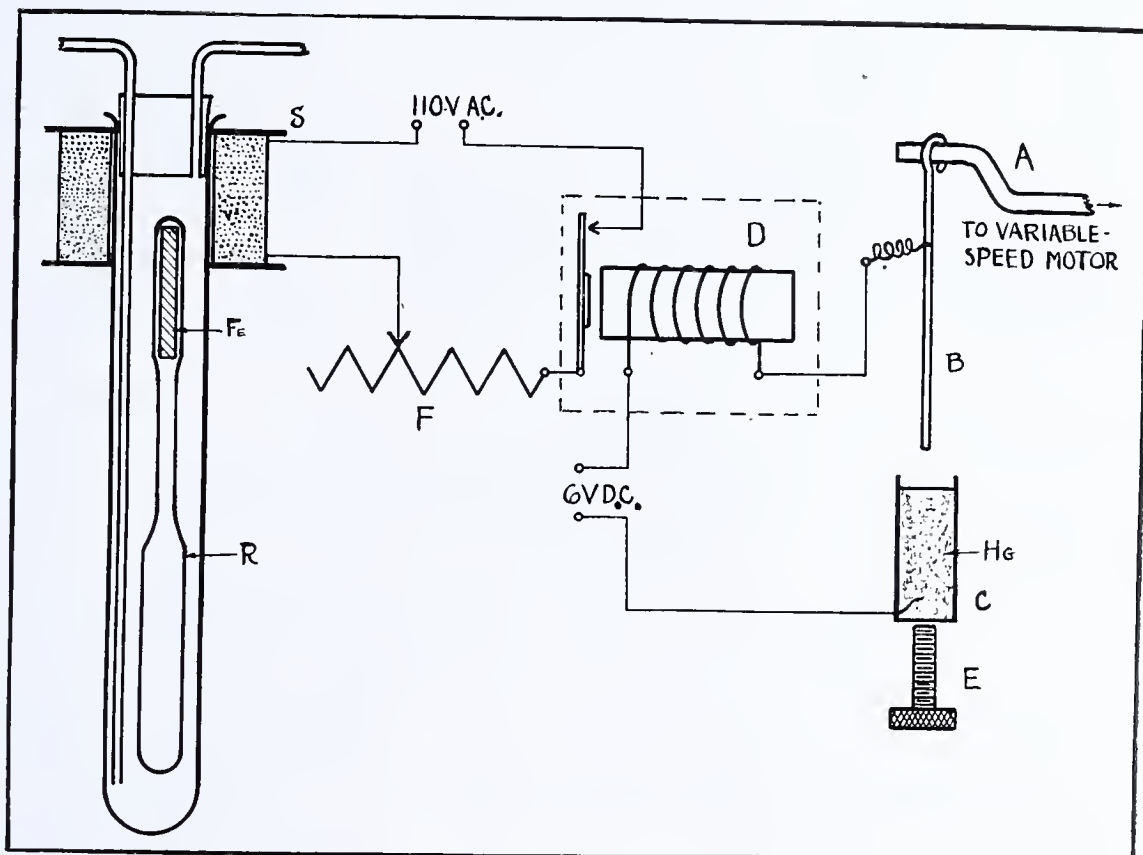
NUMEROUS internal stirrers have been devised for agitating liquids in closed systems. Most of these are of the magnetic type which require a rotating field outside the reaction flask. This is very cumbersome and impractical when the reaction flask must be kept in a constant-temperature bath, particularly when the temperatures desired require the use of a vacuum flask. The apparatus described below—

a solenoid stirrer—is very simple to construct and has proved practical and convenient for solubility determinations in non-aqueous solvents from which moisture must be excluded. This type of stirrer can be used in small cells, such as test tubes, in which a mercury-seal stirrer would be impractical. The solenoid, controlled by a make-and-break device, is placed about the upper part of the cell. It alternately raises and lowers the glass stirrer, the upper part of which encloses an iron core.

Referring to the diagram, a variable-speed motor turns a crank, *A*, which raises and lowers a copper rod, *B*. Contact is made and broken in the 6-volt circuit by dipping *B* into a mercury cup, *C*. Relay *D*, provided with graphite contacts, makes and breaks contact in the 110-volt circuit. A solenoid, *S*, lifts and drops a stirrer, *R*.

For optimum results with this type of stirrer, which is partially buoyed up by the solution, it is necessary to synchronize the frequency of stirring with the period of vibration of the stirrer in the solution. To accomplish this, it is essential to control not only the frequency with which contact is made, but also the duration of contact. The frequency can be controlled by varying the speed with which crank *A* revolves, and the duration of contact is controlled by raising or lowering mercury cup *C* with an adjustment screw, *E*. The amount of current flowing (approximately 1.5 amperes) through the 110-volt circuit can be controlled by the variable resistance, *F* (60 to 80 ohms).

The stirrer was made from a thin-walled test tube, 15 × 1.2 cm. (6 × 0.5 inch), drawn out as indicated. In the upper end of the stirrer was sealed a small bundle of soft iron wire, 3 × 0.4 cm. (1.25 × 0.125 inch). The total weight of the stirrer was about 6 grams. The solenoid consisted of 720 turns of No. 24 enamel-covered copper wire, wound on a flanged metal spool 3.5 cm. (1.5 inch) in length, through which the solubility cell passed. The solubility cell itself was a large test tube, 20 × 2.5 cm. (8 × 1 inch).

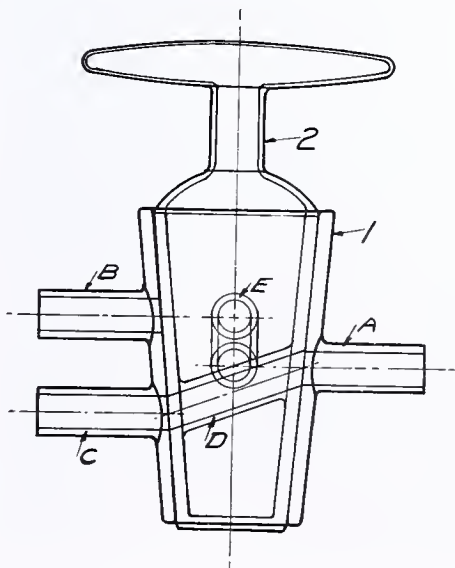


## An Improved Three-Way Stopcock

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THREE-WAY stopcocks with two stems on one side and one on the other as shown on the attached drawing are often not only useful but indispensable in a piece of apparatus. This type of stopcock in the conventional design has the disadvantage of having

the two holes through the plug so close together that troublesome leaks often develop. This has been overcome by placing holes *E* and *D* through plug 2 at right angles to each other, which means that the openings are spaced 90° apart. A further advantage is that a one-quarter turn of the plug will change the direction of flow from *C* to *B* when *A* is the inlet.





# An Electron Tube Direct Current Voltmeter of New Design

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**E**LECTRON tube voltmeters employed for electrometric measurements can be classified in two types: battery-operated and line-operated.

Battery-operated voltmeters are characterized by high stability and relative simplicity of design (1, 3). Their principal disadvantage has been the inconvenience and cost of frequent battery replacement due to a relatively high current drain. This disadvantage has prompted the design of line-operated voltmeters (2). Battery replacement is eliminated but only at the expense of circuit simplicity, initial cost, and stability with the added disadvantage of operational and constructional complexity.

portioning the current between plate and grid 2. A potential on grid 4 causes an increase in the plate current and a simultaneous reduction of current in grid 2. The "unbalance" of the bridge is consequently almost doubled.

The free grid potential of grid 4 is within the range of the voltage of the filament. The customary C-battery is thus eliminated. The proper bias is secured from the filament battery by means of potentiometer  $R_1$ .

$B_1$  is an ordinary 1.5-volt dry cell. For space economy a small type of cell such as the Burgess 4FH is recommended.  $B_2$  is a small 45-volt battery.

## Operation as a Titrimeter

Operation is extremely simple. With switch  $S_1$  to the left (Figure 1) the titration cell is connected to the binding posts. To

post 1 is connected the electrode which will increase in negative potential as titration proceeds. When this procedure is followed, meter readings increase as the titration progresses. Closing switch  $S_2$ , mounted on  $R_4$ , turns the current on. Further rotation of the knob reduces resistance  $R_4$ . This should not be done at once; instead  $R_1$  should first be adjusted until the meter reads zero. Then  $R_4$  can be advanced, thus increasing the sensitivity of the meter to any desirable value. Optimum sensitivity to be used depends upon the particular titration. It can be found only by trial and is that position of  $R_4$  which will cause the meter just to deflect over the full range during the complete titration. It is consequently advantageous to provide  $R_4$  with a scale to permit resetting to some recorded value. A scale on  $R_1$  is also of advantage.

The complete instrument is shown in Figure 2. The entire

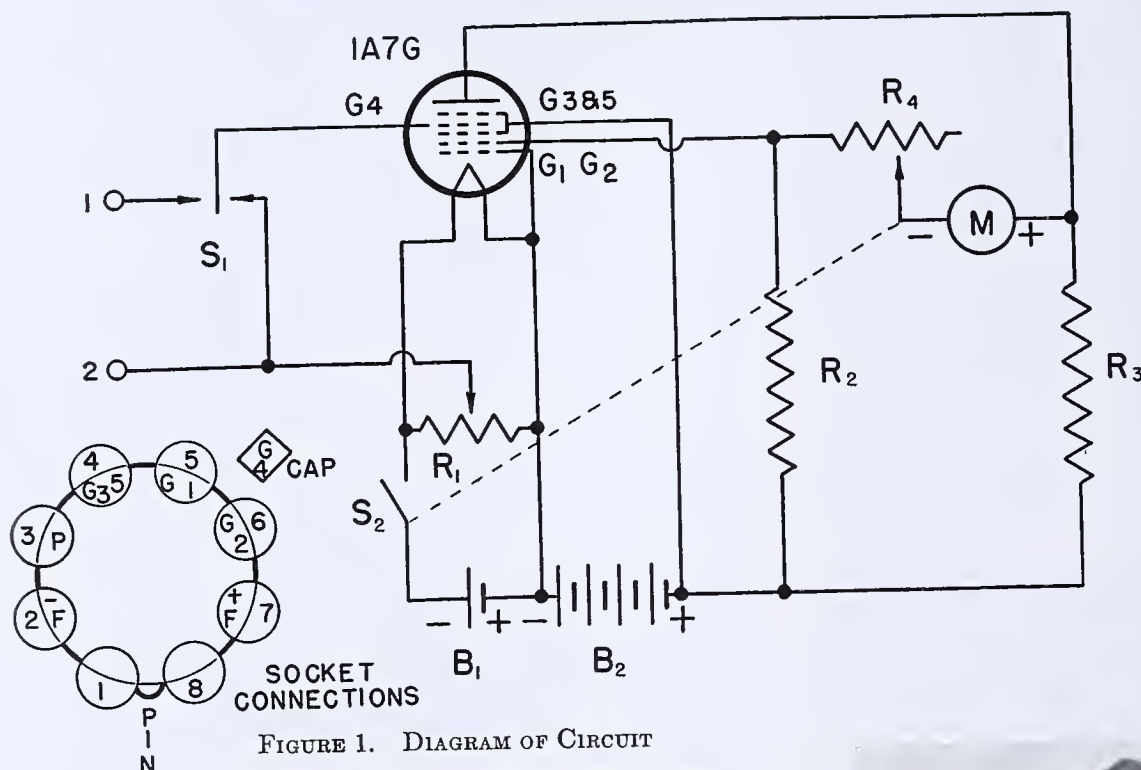


FIGURE 1. DIAGRAM OF CIRCUIT

- $R_1$ . 1000-ohm uniform volume control IRC 11-108
- $R_2$ . 2000-ohm 0.5-watt IRC BT 1/2
- $R_3$ . 2500-ohm 0.5-watt IRC BT 1/2 or 5000-ohm semivariable
- $R_4$ . 50,000-ohm volume control IRC 13-123 with switch cover plate for  $S_2$  IRC-21
- $S_1$ . S. P. D. T. switch, Yaxley 732
- $S_2$ . S. P. D. T. switch, Yaxley 732
- $B_1$ . Burgess 4FH, 1.5 volts
- $B_2$ . Burgess W30BP, 45 volts
- $M$ . Weston 0-50 microamperes, Model 801

In spite of these difficulties the trend in late years has been in the design of line-operated equipment (4-8). However, the recent introduction of a new series of 1.5-volt tubes with an exceedingly low filament current makes possible the construction of a much improved battery-operated voltmeter. By using a circuit wholly new in principle greater stability is obtained and operation is much simplified. This construction, in addition, makes possible a net reduction in the number of component parts for the complete assembly; and the low power consumption (0.3 watt) eliminates the principal objection to battery operation.

The circuit is shown in Figure 1. It consists of the pentagrid converter 1A7G in a bridge circuit. The arms of the bridge are (1) the effective cathode to plate resistance, (2) the plate load,  $R_3$ , (3) the effective cathode to grid 2 resistance, and (4) the load resistance,  $R_2$ . The meter,  $M$ , reads the condition of balance of the bridge.  $R_4$  controls the sensitivity of the meter and hence of the voltmeter as a whole.

Grid 4 controls the electron stream, not in the conventional manner of changing the magnitude of the current but by ap-



FIGURE 2. PHOTOGRAPH OF INSTRUMENT



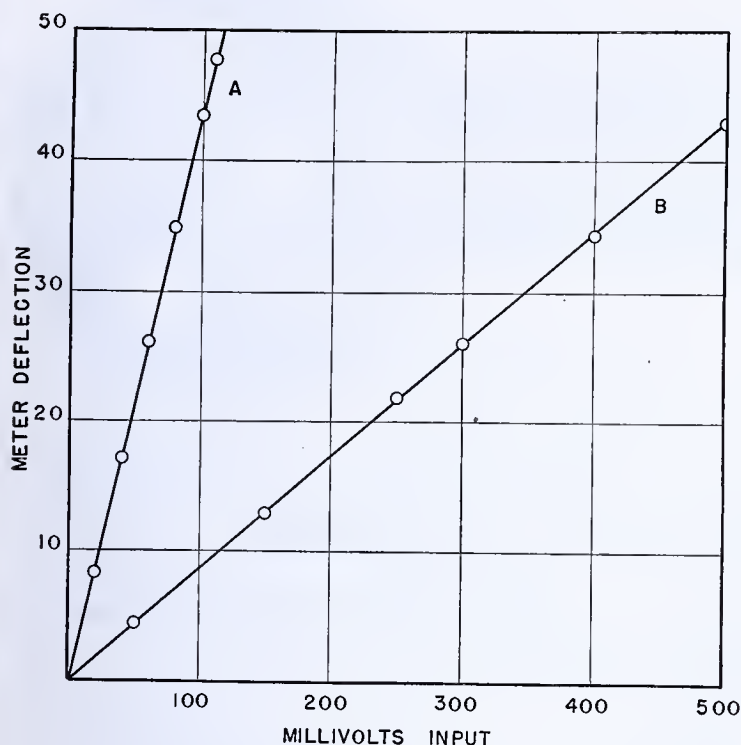


FIGURE 3. PLOT OF INPUT VOLTS AGAINST METER READING

unit is housed in a cabinet  $5.5 \times 6 \times 5.5$  inches—no larger than the familiar internal lamp and scale galvanometer. The total weight is less than 3.5 kg.

In rare instances the titration cell will develop such a high potential that it becomes impossible to secure a zero meter reading by adjusting  $R_1$ . In such a case the input leads to the posts should be reversed and  $R_1$  adjusted until a maximum meter reading is obtained. As the titration proceeds meter deflections will decrease. If control is not secured in this manner, a battery should be connected in series with the titration cell to reduce the total voltage to a workable value.

### Operation as a Voltmeter

When the instrument is to be used as a voltmeter and not as a titrimeter, original adjustment of  $R_1$  should be made with switch  $S_1$  thrown to the right. The meter will read zero for zero external potential.  $S_1$  is then thrown to the left to read the potential imposed upon the input binding posts.

A plot of input volts against meter readings is shown in Figure 3. Curve A was taken at full sensitivity and shows that full-scale deflection may be obtained by an input voltage of 100 millivolts. A higher sensitivity may be obtained by doubling the values of  $R_2$  and  $R_3$ . Curve B shows the operation of the unit at reduced sensitivity. If only the latter sensitivity is required a 0–500 microammeter may be used instead of the 0–50 microammeter unit indicated in Figure 1. The meter should be connected with the positive terminal to the plate lead, so that increasing the negative voltage at grid 4 will increase the meter reading. The value of  $R_2$  has been chosen to give a zero reading on the bridge meter when the grid is left free. Because of variations in tubes, the specified value of  $R_2$  may not produce these same results with all tubes. If the free grid deflection is less than zero the resistor need not be changed, since the grid potential in operation will always be more negative than that at free grid. If this is not the case the value of  $R_3$  must be increased until the desired meter reading is obtained. The proper selection is best made after the tube has been allowed to age about 24 hours.

### Stability

Erratic fluctuations are occasionally visible only when the unit is operating at full sensitivity, and thus correspond to

input voltages of the order of  $10^{-4}$  volt. The steady drift after the initial warming-up period is of the order of millivolts per hour and is therefore negligible for all titration measurements.

### Grid Current

The grid current is very low ( $10^{-10}$  ampere) and does not change abruptly from the free grid value as is usually the case with conventional receiving tubes. The grid current is directly proportional to the grid voltage, which indicates that it is due to leakage in the apparatus and to positive ion current within the tube.

### Battery Life

In ordinary daily operation a set of batteries should last 6 months; thus the cost of battery replacement is less than 25 cents per month.

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## Continuous Supply of Hot Distilled Water

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**I**N CONNECTION with the course in qualitative and quantitative analysis at the Massachusetts Institute of Technology, it has become necessary to use large quantities of hot distilled water. The idea of a continuous supply of hot distilled water seemed desirable, and upon investigating the various possibilities the following method was chosen and subsequently installed.

The installation consists of a 113.5-liter (30-gallon), gas-fired Whitehead automatic water heater containing a Monel tank. Thermostatic controls are an integral part of the unit and the Monel tank is well insulated. All brass pipe, elbows, valves, and faucet were well tinned on the inside previous to installation.

The temperature of the water is regulated for  $85^\circ\text{C}$ . This temperature is maintained satisfactorily during a period when 60 to 90 liters of hot water are drawn off within about 3 hours.

The following test was made to determine the purity of the hot distilled water. With the unit in operation, maintaining a temperature of  $85^\circ\text{C}$ ., no water was drawn off for a period of about 60 hours. A 10-liter sample was taken, evaporated to a small volume, and analyzed to give 0.35 mg. of nickel per liter of water. No copper was found in this 10-liter sample.

The amount of nickel introduced into the distilled water is not considered to be significant except in special work. The unit requires no attention, has proved very satisfactory, and the cost is nominal.



# MICROCHEMISTRY



## Determination of Lead by Dithizone

### Modifications and Improvements of the Hubbard-Clifford-Wichmann Method as Applied to Biological Material

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**D**ITHIZONE has been used in this laboratory for the past three years as a reagent for the determination of lead in biological material, and the experience gained in about ten thousand lead analyses has led to certain modifications and improvements in the method reported by Hubbard (7), who based his photometric dithizone procedure upon work done by Clifford and Wichmann (6) and by Wilkins, Wiloughby, Winter, and their co-workers (10, 11, 12). The improvements described in this paper have made possible increased accuracy and a saving of time, and have resulted in keeping the rack blank down to the very low figure of 0.1 microgram.

#### Apparatus

The apparatus employed is essentially the same as that described by Hubbard (7). The performance of the neutral wedge photometer, however, has been improved by a few changes. A small compensating wedge of Bausch & Lomb neutral "C" glass has been placed in the light path, as suggested by Clifford (5), in order to make the comparison fields of the instrument "shade off" similarly. In addition, the compound gelatin filter has been replaced by a permanent glass filter with maximum transmission at 510 millimicrons. These changes necessitated a stronger light source and accordingly 50-candlepower bulbs have been substituted for the 32-candlepower bulbs originally used.

A very convenient device, suggested by R. R. McNary, of this laboratory, consists of special rotary funnel racks (Figure 1) fitted with opaque glass bases. The metal rings which hold the funnels have been rubber-plated by the Anode process. This rubber covering resists the reagents used in the analysis much better than any type of paint available.

Glassware and other equipment used are similar to that described by Hubbard (7).

#### Reagents

Ammonium citrate solution (40 grams of citric acid per 100 ml.) is delead by shaking it with dithizone in chloroform after sufficient ammonium hydroxide has been added to make the solution alkaline to phenol red.

Potassium cyanide solution is rendered lead-free by the following procedure:

A substantially saturated solution containing 50 grams of potassium cyanide in sufficient water to make 100 ml. is repeatedly shaken with portions of dithizone in chloroform (30 mg. per liter) until the lead is removed. Part of the dithizone dissolves in the aqueous phase but sufficient remains in the chloroform to color it and to indicate when the lead has been completely extracted. Most of the dithizone in the aqueous phase can be removed, if desired, by repeated extractions with pure chloroform. The strong potassium cyanide solution is then diluted with redistilled water to the proper strength (10 grams per 100 ml.). It is not necessary to filter the solution. (If instead of the concentrated solution, the final one is shaken with dithizone in chloroform in an attempt to delead it, the increased alkalinity of this dilute solution causes the removal of all the excess dithizone from the chloroform and renders the complete extraction of the lead more difficult.)

Hydroxylamine hydrochloride solution (20 grams per 100 ml.) is made substantially lead-free as follows:

Twenty grams of hydroxylamine hydrochloride are dissolved in sufficient water to make about 65 ml. and a few drops of *m*-cresol purple indicator solution are added. Concentrated ammonium hydroxide is next added until a yellow color results. Sodium diethyldithiocarbamate in water (an approximately 4 per cent solution) is added in sufficient quantity to combine with all the lead (and most other metals) present and to leave a considerable excess. After a few minutes the organo-metallic complexes and the excess reagent are completely extracted with chloroform. The absence of a yellow color in the chloroform when a portion of the chloroform extract is shaken with a dilute solution of a copper salt indicates when this point is reached. Redistilled hydrochloric acid is then added to the hydroxylamine hydrochloride solution until the indicator turns pink, and redistilled water is added to make the final volume 100 ml. It is not necessary to filter the solution.

Other reagents are purified as described by Hubbard (7).

By using these carefully purified reagents and avoiding other sources of contamination (such as removing dust in the room by air filtration) it has been possible to show a rack blank of not more than 0.1 microgram and to keep this blank consistently low from day to day. Obviously, a consistently low blank increases the significance of analytical results when the sample contains only a small quantity of lead (below 10 micrograms). Since fecal samples are prepared for analysis by dry ashing, the rack blank of 0.1 microgram represents the total blank for such analyses, and if redistilled acids are used for the preparation of other types of samples, the total blank



may also remain in the order of 0.1 microgram. However, in practical routine work where large quantities of acid are used to prepare large samples of urine and mixed foods, the reagent acids used are restricted to uniform lots which are analyzed periodically, and a small blank results from the acid used in the preparation of the sample.

The author believes that the blank of 0.1 microgram is the lowest consistent figure so far reported for this type of lead analysis.

### Experimental

Clifford and Wichmann's method (6) is not directly applicable to the analysis of certain biological material containing bismuth or large amounts of inorganic salts, such as feces and mixed foods. Inorganic salts often interfere by oxidizing the dithizone in the initial extraction, thus preventing the choice of the proper standard dithizone solution to be used in the photometric step. In addition, small amounts of salts may be entrained by the dithizone-chloroform solution in the first extraction and cause interference in the latter part of the analysis. Because of these factors Hubbard (7) found it necessary to use two extractions in isolating the lead and choosing the proper standard dithizone solution. He also tested each sample for bismuth and removed it if present.

It has been reported (1) that the oxidation of dithizone in the first extraction referred to above could be eliminated by the use of hydroxylamine hydrochloride. This would make possible a shortened procedure, in which the lead could be estimated roughly in the first extraction. However, it was felt that hydroxylamine might reduce the tin which is always present in feces and mixed foods so that the characteristic interference due to stannous tin would result. [As stated by Hubbard (7) and Laug (9), this interference does not normally

occur when biological samples are prepared by the usual oxidizing methods.] In order to determine whether hydroxylamine would cause interference when used in analyses of this type in the presence of tin, prepared samples of feces and mixed foods were analyzed by Hubbard's method with and without the addition of hydroxylamine, and were also analyzed for tin and lead by the spectrographic method used in this laboratory (3). An inspection of Table I shows that hydroxylamine did not affect the results, although the spectrograph showed the presence of relatively large quantities of tin.

TABLE I. EFFECT OF HYDROXYLAMINE

Sample	Lead (Hubbard's Method) <sup>a</sup>		Spectrographic Method	
	Without hydroxylamine Mg.	With hydroxylamine Mg.	Lead Mg.	Tin Mg.
Food, 1886	0.16	0.16	0.16	3.75
Food, 2198	0.34	0.34	0.35	7.8
Feces, 2243	0.56	0.55	0.56	3.0

<sup>a</sup> Aliquots of one tenth of the sample were used.

Salts entrained by the chloroform in the first extraction often make uncertain the bismuth test as described by Hubbard. This has been recognized by Hubbard in his work on a dithizone method for the determination of bismuth (8). These interfering salts, however, can be removed by washing the dithizone-chloroform extract with water; if this is done, tests have shown that as little as 3 micrograms of bismuth can then be detected by the routine test.

Since no citrate is used in the second extraction step in Hubbard's method, occasional samples high in both lead and phosphate may present difficulties due to the fact that phosphate entrained by the chloroform and carried over to the aqueous phase of the second extraction may cause the precipitation of lead phosphate. The loss will not take place if sufficient dithizone solution to extract most of the lead is added immediately after the nitric acid solution is made alkaline. In the modified method here presented this precipitation of lead phosphate cannot occur.

The loss of lead which takes place when the mixed color is not developed immediately after the addition of the ammonia-cyanide mixture has been attributed by Clifford (4) to the presence of phosphate as an impurity in the potassium cyanide used. It is very likely that the phosphate causing the interference is often due not only to the potassium cyanide but also to entrainment by the chloroform in the first extraction.

So far thallium has not been encountered in samples of biological material and no attempt has been made to include a test for its presence in the routine method. In many analyses the absence of thallium has been confirmed by spectrographic observations.

### Modified Method

**PREPARATION OF SAMPLES.** Samples are treated as previously indicated (3, 7).

**ISOLATION OF LEAD.** The procedure is similar to Clifford and Wichmann's and to Hubbard's but manipulative changes have been introduced and the method has been shortened.

The aliquot of the prepared sample is treated as described by Hubbard, except that 1 ml. of deaerated hydroxylamine hydrochloride solution is added to each sample after the addition of



FIGURE 1. ROTARY FUNNEL RACKS



the ammonium citrate. The lead extraction is started with 5 ml. of dithizone solution and the color is noted in order that the proper standard dithizone solution may be chosen in the final lead estimation. (The lead usually is not extracted quantitatively with each portion of dithizone solution, because of the various salts present. Instead of 50 micrograms of lead, usually only 40 micrograms will be extracted by each 5 ml. However, with practice the quantity of lead actually present can be estimated from the color of the dithizone solution with surprising accuracy. When the quantity of lead present is less than 10 micrograms this is recognized by the distinctive greenish blue color of the 5-ml. portion of dithizone solution.)

TABLE II. CHECK ANALYSES

Lead Added Micrograms	Lead Found Micrograms
0	<0.2
5	5.0, 5.1
25	25, 24.5
50	50, 49.5
75	75, 74
100	100, 100

After the initial portion of the dithizone solution has been drained into another funnel, successive 5-ml. portions are added until the lead is completely extracted. The color of each portion is noted in order to estimate the total quantity of lead present, as previously described. Chances for loss of lead in the analysis are decreased if the first 5-ml. portion of dithizone solution is not drained off, but is kept in the funnel while another portion is added, and the entire 10-ml. portion is then shaken with the sample and drained after the color has been noted. This 10-ml. portion usually contains most of the lead, together with some excess dithizone, and the loss of a drop in transferring to another funnel means a much smaller percentage of error than the loss of a drop from a 5-ml. portion practically saturated with lead.

The combined dithizone extract (containing entrained ammonia and salts) is washed with 50 ml. of water, which is then washed with 5 ml. of pure chloroform. This chloroform washing should be green in color; if it shows the presence of lead, the water phase should be washed with another 5-ml. portion. The chloroform is added to the dithizone extract, which is then shaken with 50 ml. of dilute nitric acid (10 ml. of nitric acid, sp. gr. 1.40, per liter) and the dithizone solution is drained off to 0.5 ml. and discarded. Three drops of *m*-cresol purple indicator solution (Clark and Lubs) are added to the nitric acid solution, and dilute ammonia is added until the orange color indicative of pH 2 is reached. The funnel is shaken vigorously and if the 0.5-ml. portion of dithizone solution shows no change in color, bismuth is absent. If bismuth is present it is extracted with successive portions of dithizone solution. The dithizone solution is then drained off, 5 ml. of pure chloroform are added, and the funnel is shaken. The funnel is allowed to stand unstoppered until the drop of chloroform floating on the surface of the dilute nitric acid has evaporated. The chloroform is then drawn off as completely as possible, but at most only a drop of the aqueous phase is allowed to enter the hole in the stopcock.

**FINAL ESTIMATION OF LEAD.** In the following part of the procedure direct sunlight should not be allowed to strike the funnels.

The proper standard dithizone solution (10 or 25 ml.) is added to the funnel containing the lead in 50 ml. of dilute nitric acid, 7 ml. of ammonia-cyanide mixture are added, and the funnel is shaken for one minute. The pressure which develops should not be released through the stopcock; instead the stopper should be lifted. One can thus avoid blowing water into the funnel stem. If a number of analyses are being run, the mixed color can be developed in the whole series of analyses and photometric readings taken one after the other. Experiments have shown that the mixed color is stable for at least 5 hours.

Part of the dithizone solution (2 ml. of the 0- to 10-microgram solution, 10 ml. of the 0- to 50-microgram solution, or 15 ml. of the 0- to 100-microgram solution) is used to flush the stem of the funnel, the end of the funnel stem is dried, and the solution is allowed to run directly into the cell for the photometric reading. Since the 0- to 10-microgram cell holds the entire 8 ml. remaining in the funnel, it cannot be rinsed with part of the dithizone solution, but must be cleaned and dried with pure acetone after each sample. The other two cells, however, can be rinsed with dithizone solution at least twice and it is rarely necessary to dry them with acetone between samples.

The working curves to which the photometric readings are referred are made as described by Clifford and Wichmann (6) and Hubbard (7), except that the 50 ml. of dilute nitric acid con-

taining the known amount of lead are brought to pH 2 before adding the 7 ml. of ammonia-cyanide mixture.

Discussion

A comparison of this modified method and the procedure given by Hubbard (7) will show certain manipulative changes. Some of these have resulted in a saving of time, so that a chemist, with the help of a technician for 4 hours, can now analyze forty prepared samples in 7 hours.

As a check on the accuracy of results given by the modified method, analyses were made of samples of delead synthetic urine salts similar to those used in spectrographic work (2), to which had been added quantities of lead unknown to the analyst. The results are shown in Table II.

A number of routine analyses of urine, feces, mixed foods, and blood were made by Hubbard's method and by the modified procedure. Results by the latter procedure averaged about 3.5 per cent higher, especially when more than 10 micrograms of lead were present (Table III).

TABLE III. COMPARISON OF METHODS

Sample	Lead Found	
	Hubbard's method Micrograms	Modified method Micrograms
Urine		
4847	28	28
4849	13	13.5
4883	5.2	4.9
4897	4.8	4.9
4917	28	28.5
Feces		
4771	95	96
4781	43	45
4785	92	94
4799	39.5	41
5064	38	40
Foods		
3979	29.5	30
4018	36	36.5
4438	46	46
4575	39.5	41.5
4729	96	99
Blood		
5052	2.3	2.6
5110	4.0	4.0
5111	2.8	3.0
5203	2.8	3.0

This increased recovery of lead can probably be attributed to the smaller number of manipulations in the modified method. However, the loss occurring in Hubbard's method, which has been noticed in various experiments during the past year, is so slight that it is of very little practical importance. The modified method almost entirely corrects this tendency to give slightly low results, although no recent analysis of a known quantity of lead above 10 micrograms has been on the high side.

TABLE IV. LOSS OF LEAD

Lead Present Micrograms	Lead Found in Usual Analysis Micrograms	Lead from Aqueous Phase and from Acid- Washed Dithizone Micrograms
100	99	0.3
100	100	0.1
100	100	0.2

Although it has been stated that dithizone extracts lead quantitatively from aqueous solutions at the proper pH, it was felt that a small portion of the lead in a sample of biological material might be rendered nonreactive by large amounts of phosphates and other salts. To check this, the sample of synthetic urine salts containing 100 micrograms of lead (Table II) was run in triplicate. The aqueous phase after the first extraction was acidified, made alkaline, and immediately re-extracted with dithizone. The lead resulting from this treatment, plus any lead recovered by a second acid wash of the dithizone solution originally containing the 100 micrograms of lead, is shown in Table IV.

This indicates that no significant loss of lead in the two solutions can be detected by dithizone.



### Summary

The following modifications and improvements have been made in the dithizone method for the determination of lead in biological material described by Hubbard:

The use of hydroxylamine in the initial extraction prevents the oxidation of the dithizone and permits the elimination of the second extraction step of the Hubbard method.

Washing the first chloroform extract removes extraneous entrained salts and improves the test for bismuth.

Filtrations through cotton and through paper have been eliminated from the procedure without loss of accuracy, and with a resultant saving of time and decrease of opportunities for contamination.

The addition of the standard dithizone solutions and the development of the mixed color in all the samples of a series before the photometric readings are made save time and do not affect the accuracy of the analyses.

Purification of reagents and elimination of contamination have made possible a blank of 0.1 microgram, which is believed to be the lowest yet reported.

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## Refractive Index Measurements in Qualitative Organic Microanalysis

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WITH the recent developments of Foulke and Schneider (2, 5) in adapting the methods of Kamm (3) and others to use on a micro scale, the last major field of analytical activity—qualitative organic analysis—begins to yield to micro treatment. It will always be less practical to prepare and identify confirmatory derivatives with minute samples than with the customary amounts; hence as large a number as possible of physical properties will be advantageously determined on the micro scale. It is desired in this communication to emphasize the ease and wide utility of refractive index measurements for use in connection with such schemes as that of Foulke and Schneider, and by means of a few examples to show how effectively this measurement can supplement the conventional boiling and melting point determinations, particularly in dealing with liquid samples.

The methods used for determination of indices of refraction of liquids were those of Chaulnes (6) and of Edwards and Otto (1). Since the latter method was found to be accurate only to about  $\pm 0.003$ , the measurements reported were obtained with the former method, which could be made somewhat more sensitive, though it required slightly larger samples.

A hole about 5 mm. in depth was drilled approximately 1 cm. from the edge of a piece of clear plate glass about 6 mm. thick, using a steel drill 1 mm. in diameter. The drill was rotated slowly and kept wet with turpentine at all times. A smaller drill might equally well be used and for economy of sample the hole might not be so deep; but if much smaller samples must be used, the Edwards and Otto refractometer is more practical. The bottom of the hole was polished with tripoli compound to prevent light diffraction, and on this polished bottom a scratch was made by inserting a small crystal of silicon carbide and rotating the drill slightly.

The empty cell with cover slip was placed on a microscope stage, the scratch brought into sharp focus, and the fine-adjustment setting noted. The cell was filled with the liquid to be tested and the cover slip slid on and pressed down simultaneously, using an eraser on the end of a pencil. The scratch was again brought into sharp focus with the fine adjustment and the reading taken. The cell was calibrated with a series of liquids of known refractive index, plotting refractive index against fine-adjustment readings.

The cell was kept completely clean and dry by using a series of fine capillaries to flush the cell with wash liquids and finally to draw through a stream of air for drying. The presence of a

film of liquid led to lack of reproducibility of the zero reading, which then became the criterion of dryness.

TABLE I. LIQUIDS TESTED

B. p. ° C.	Liquid	Dis- place- ment	Deter- mined Index	Hand- book Index Value	Accuracy to within:
100	Formic acid	276	1.373	1.371	0.002
100	n-Butyl chloride	295	1.410	1.412	0.002
145	Ethyl orthoformate	287	1.394	1.392	0.002
145	Ethyl chloroacetate	297	1.414	1.412	0.002
77	Ethyl acetate	276	1.373	1.373	0.000
78	Ethyl alcohol	269	1.360	1.361	0.001
54	Ethyl formate	269	1.360	1.360	0.000
55	Acetyl chloride	285	1.391	1.390	0.001

The use of refractive index determined by immersion methods is equally applicable to the identification of solid compounds. The values for organic solids have not been so well collected as have those for liquids (4) and are yet to be determined in many cases. However, if a polarizing microscope is used, most crystals (being anisotropic) will readily yield two refractive indices in different directions without other special equipment. Biaxial crystals with three refractive indices cannot usually be readily oriented to determine the third value. The two easily determined indices will in most cases make positive identification possible when used in conjunction with solubility determination, elementary composition, and melting point. Much investigation of the refractive indices of solid organic compounds needs to be carried out in order to make this very useful property generally applicable to the identification of these materials.

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# A Needle Valve for the Micro-Dumas Determination of Nitrogen

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ONE of the most important manipulative details of Pregl's micro-Dumas determination of nitrogen is the adjustment of the stopcock between the combustion tube and the azotometer. Pregl emphasizes this by the statement (2), "This adjustment of the stopcock is probably the only feature of the manipulation in this determination which requires some practice, as it must be so carried out that the above-mentioned velocity of the gas current is not exceeded for even a few seconds."

bustion tube at the beginning of the analysis is best performed before connecting it to the azotometer and valve.

Besides controlling the flow of gas under the very slight pressures existing during the nitrogen analysis, this valve may be used in other applications under much more severe conditions and in instances where its transparency is an asset. Tests have shown that no leakage occurs at pressures up to 25 pounds per square inch and that, while care must be used to avoid excessive force in closing the valve, it is rugged and will give long service.

## Construction

The taper of the glass seat is approximated by eye during the glass working. The needle is ground in with 500- to 700-mesh silicon carbide suspended in water, finishing with "flour" of the same material. During the grinding operation the needle may be centered in the glass body by means of the bushing, *C*, which is allowed to turn freely with it. A small stirring motor equipped with a chuck is convenient as the source of power. While grinding, the needle should be lifted frequently from the seat, and heating of the glass due to excessive pressure must be avoided. If fine cracks develop it is an indication that the needle is being pressed in too hard, or that the speed of rotation is too high. The final lapping-in with "flour" should be done by hand.

The stem, *E*, is of 18-8 stainless steel and the knurled handle, *F*, is of brass in two sections which are threaded and tightened against each other. The U. S. Standard of 48 threads per inch gives satisfactory regulation, but considerable variation in pitch is allowable.

Bushing *C* is made from 0.156-inch (3.97-mm.) soft steel rod, counterbored 0.375 inch (9 mm.) with a 0.116-inch (2.95-mm.)

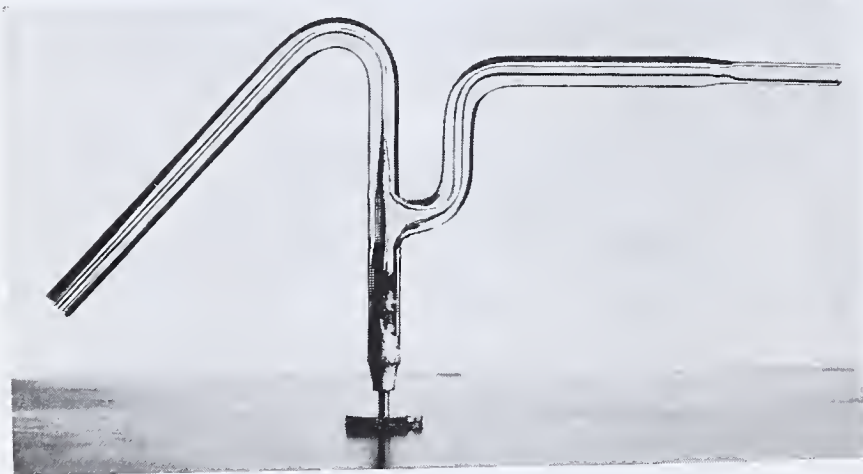


FIGURE 1. ASSEMBLED VALVE

Despite this emphasis no attempt has been made to improve this gas-control device other than to file grooves in the stopcock barrel, or to use a screw adjustment on the elongated handle (1). It has been the authors' experience that the stopcock is unsuited for the close metering of a gas stream and the needle valve described below has proved decidedly superior, both in this and in other laboratories.

To determine the performance and reliability of this valve in other hands before publication, samples of an earlier type were sent to L. F. Small of the University of Virginia, to N. L. Drake of the University of Maryland, and to H. K. Alber of the Biochemical Research Foundation of the Franklin Institute in Philadelphia.

All these valves worked well, but in two cases mercury leaked past the threaded portion of the stem. A method for overcoming this difficulty was worked out and an improved valve of the type here described was sent to Professor Drake, who subsequently reported very satisfactory results, even in the hands of students. The authors wish to express their thanks to these men for their kind and valued cooperation.

The valve, shown complete in Figure 1 and in detail in Figure 2, is composed of a Pyrex glass body, *A*, and a stainless-steel needle, *E*. A threaded steel bushing, *C*, contains a packing gland, *D*, consisting of a short piece of paraffin-impregnated rubber tubing which effectively lubricates and seals the stem against leakage of mercury. The glass side tubes can be bent to fit the requirements of any apparatus, so long as the part containing the mercury is kept nearly vertical. Since this valve has one less function than the three-way stopcock which it replaces, the operation of sweeping out the com-

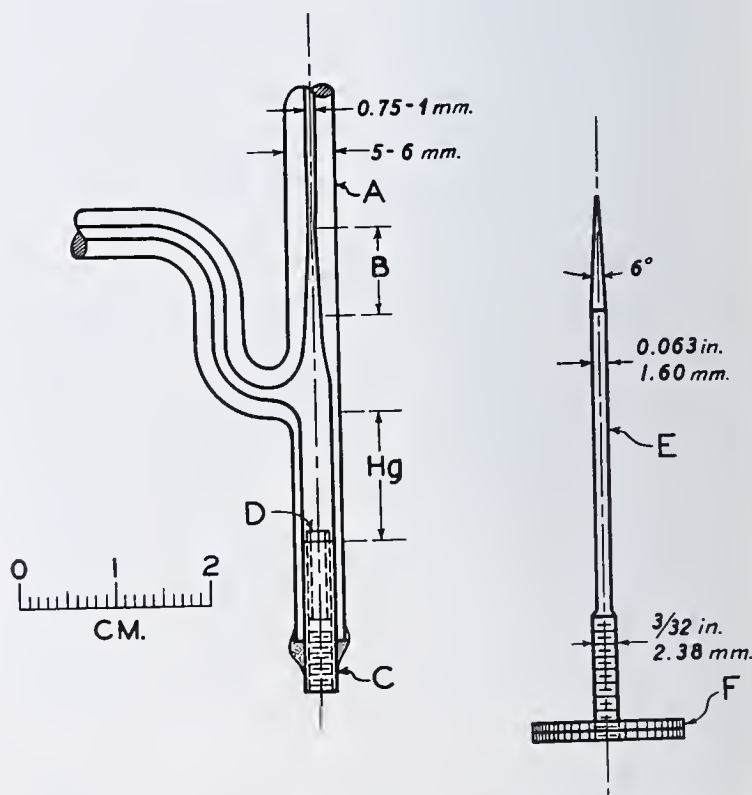


FIGURE 2. DIAGRAM OF VALVE



hole. Rubber tubing 0.0625 inch (1.6 mm.) in diameter (spectacle tubing) is used for packing *D*, and is pretreated by immersing it in hot paraffin for 10 to 15 minutes and allowing it to swell to fit the hole counterbored in *C*. Because of variations in size of this type of tubing, the diameter of the hole in the bushing and the degree of swelling cannot be stated very exactly, and some experimentation is necessary with each piece of tubing. No adhesive is necessary to hold the rubber in place, since the comparatively rough inner surface of the hole offers considerably more resistance to rotation than does the polished valve stem.

Sealing wax (Dennison's No. 391) is used to cement bushing *C* into the glass body, *A*.

Mercury is placed in the portion marked *Hg* to act as a positive liquid seal, and to eliminate dead space.

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# Handling of Hygroscopic Substances

## In the Microchemical Determination of Carbon and Hydrogen

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THE various drying devices which have been described in the literature for use in determining the amount of water in the microchemical analysis of a substance of type *C* (*I*) are oftentimes unsatisfactory when the anhydrous material is to be analyzed. The apparatus described below consists of a jacketed drying tube, so arranged that it may be kept at constant temperature, and a weighing bottle of special design. The sample is dried, weighed, and introduced into the carbon and hydrogen combustion tube without coming in contact with moisture at any stage of the operation. Figure 1 shows the apparatus.

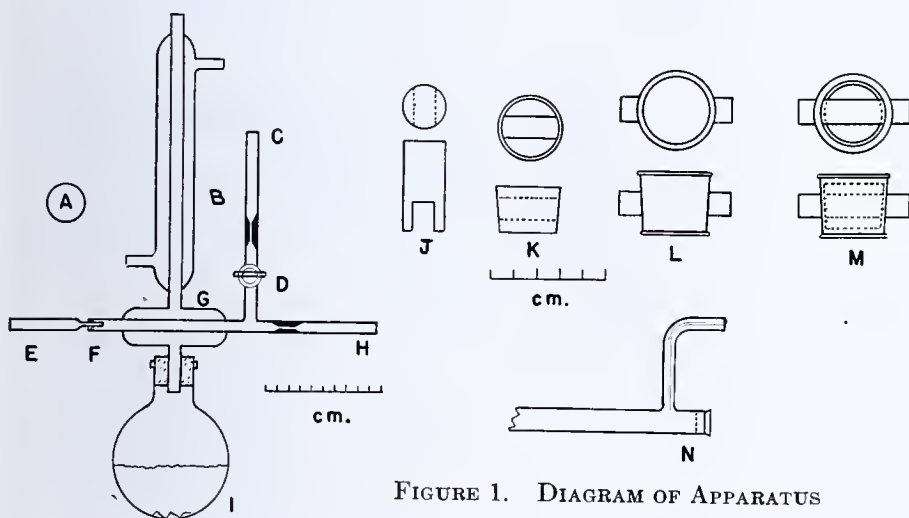


FIGURE 1. DIAGRAM OF APPARATUS

*A* is essentially a Pregl microdesiccator, modified by the addition of the jacket, *G*, and the side-arm drying tube, *C*, which is filled with anhydrous calcium sulfate (indicating Drierite). By using an appropriate liquid, it is possible to keep the temperature of the drying chamber constant over long periods of time without supervision. The adjustment of the flame is a source of trouble in the original Pregl design in which a copper block is used to maintain a constant temperature around the tube.

*M* is a weighing bottle of new design consisting of the shell, *L*, the core, *K*, and the wooden detachable handle, *J*. *L* has two short side arms of glass tubing, the same diameter as the dryer and the combustion tube, *N*. The weighing bottle is constructed of soft glass. The core is greased with a light high-vacuum stopcock grease and the excess removed by wiping. Before use, the core is rotated several times and the inner portion of the weighing bottle wiped out with cotton. This is repeated several times to ensure a clean inner surface.

The weighing bottle was tared with glass and constant weight was usually reached in 15 minutes. The weight could be decreased considerably by using a thinner rim. The following values were obtained on the empty weighing bottle, when the stopper was rotated and the bottle wiped between

each weighing. The results have been corrected for zero variations and are the weights in milligrams in excess of the tare: 9.958, 9.960, 9.966, 9.964, and 9.965.

The maximum variation from the mean is 5 micrograms. In routine analysis of hygroscopic substances the variation in weight of the weighing bottle plus boat plus dry sample was seldom over 5 micrograms.

In the course of an analysis, the weighing bottle with the empty boat is connected to *F* by means of a short length of rubber tubing which has been wiped out with glycerol and then with cotton. Air is passed through *C*, with *D* open, for a few seconds.

The core, *K*, is turned by means of the handle, *J*, until closed and, after disconnecting, the bottle is wiped and weighed in the usual manner.

The sample is placed in the boat and an approximate weight determined. The boat is now transferred to the dryer and placed midway in chamber *G*. The liquid in the flask, *I*, is boiled and refluxed in *B*. The tube, *E*, containing the same desiccating agent as in *C*, is connected to *F*, and a slow stream of dry air is sucked through the apparatus by connecting *H*, which also contains the same desiccating agent, to the vacuum line. *D* is closed during this operation. A "bleeder" may be used to obtain the desired vacuum. After the sample is dried, air is applied to *C*, stopcock *D* is opened, and air is allowed to escape through *E*. *E* is now disconnected and, while air is flowing, weighing bottle *M* is connected to *F* by means of the rubber tubing used before. The boat is removed to the center portion of the weighing bottle by means of a glass rod having a platinum hook fused into the end. Core *K* is now turned until closed off and the weight obtained as before.

After the weight of the dry sample is obtained, it is transferred to the carbon and hydrogen apparatus as follows: The stopper at *N* is removed and with dry oxygen streaming from *N* the weighing bottle is attached by means of the rubber tubing previously used. Core *K* is turned until open and the boat is pushed into the combustion tube by means of a glass rod. The weighing bottle is removed and the stopper replaced at *N*.

By this method it is possible to dry and analyze a substance, such as chrysanthemin chloride, which takes up its water of hydration almost instantaneously.

The apparatus may also be used for other purposes in microchemical analysis, when it is desired to isolate the substance from moisture and carbon dioxide of the atmosphere—for example, the determination of loss on ignition of limestone where the substance is weighed in the weighing bottle after ignition in a quartz tube.

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PRESENTED before the Division of Microchemistry at the 97th Meeting of the American Chemical Society, Baltimore, Md.



# An Improved Mercury-Sealed Micro Absorption Tube

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VARIOUS types of absorption tubes for the microdetermination of carbon and hydrogen by the combustion of organic substances have been described in the literature. The tube designed by Pregl (6), still widely used in many laboratories, is open at both ends but has constrictions in the capillary tubing to reduce diffusion during weighing. Nevertheless diffusion is great enough to necessitate replacement of

As the sealed tube is normally handled, there is no danger of the mercury's dropping through an aperture of the size specified.

When the tube is taken from the absorption train, wiped, and sealed, the tube temperature is still somewhat above room temperature; further cooling takes place during the interval of standing before weighing. If the gas pressure within the tube should be sufficiently diminished, the mercury seal would

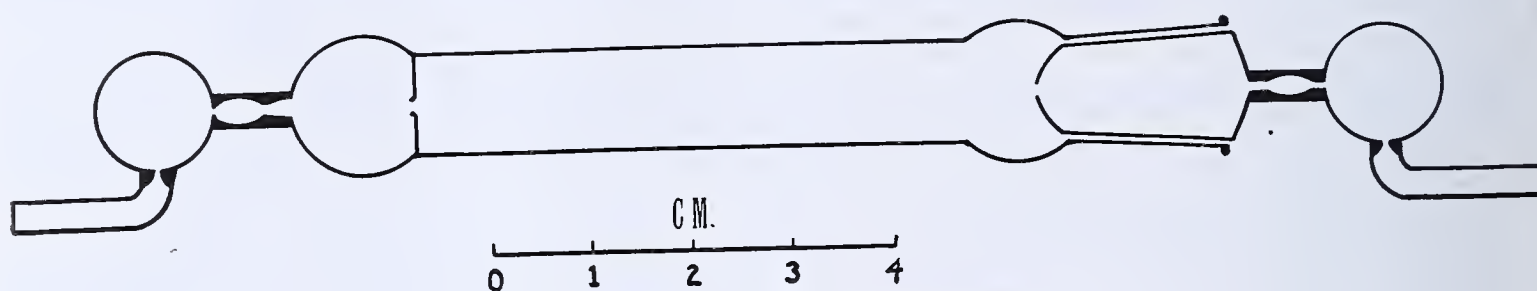


FIGURE 1. IMPROVED ABSORPTION TUBE

oxygen by air before the weighing is made. The use of a tube whose ends may be closed permits weighing while the tube is filled with oxygen and eliminates that part of the procedure dealing with the oxygen removal. This has been accomplished by fitting the tube with stopcocks (1, 3), with mercury seals (2, 5), or with steel balls (4).

Tubes with stopcocks have several important disadvantages. There is always the possibility of leakage around the stopcocks, accurate weighing is difficult because the tubes are heavy, the lubricant around the joints may pick up dust or moisture from the air, or some of the lubricant may be squeezed out and removed during wiping. Absorption tubes with mercury seals have none of these difficulties and still retain the advantage of weighing the tube without first displacing the oxygen with air. However, after the tube is sealed the mercury droplets may be dislodged if either the internal gas pressure of the tube or the atmospheric pressure changes greatly. Principally for this reason a tube sealed with stainless-steel balls was designed by Johns and found to be highly successful. The authors have used mercury-sealed tubes successfully for 10 years and feel that dislodgment of the seals by changing gas pressure need not be an important factor with tubes of proper design.

Several types of tubes have been used in this laboratory, but the design which has given the most satisfactory results is shown in Figure 1. It was made from a Pregl tube which had been purchased from a commercial supply house. Bulbs 3.0 to 3.5 cm. in diameter were blown in the capillary tubing at the positions shown. Tubing 3.0 to 3.5 mm. in external diameter was joined to the side of the bulb and bent as indicated, and at the junction of the tubing and the bulb a constriction about 0.25 mm. in diameter was made. This is small enough to retain the globule of mercury (2 to 3 mm. in diameter) which rests there when the tube is sealed, but large enough to permit the flow of oxygen through the unsealed tube when in use in the absorption train.

be broken momentarily and air sucked in before the seal again fell into place. Normally this does not happen and the slightly different buoyancy is compensated by making the blank determination with the identical technique. It is impossible for the mercury droplets to be sucked into the tube; this objectionable feature is restricted to the Cornwell type of tube. In view of the normal tendency of the tube to cool before the weighing is made, this is an important point; on the other hand, if the sealed tube should be heated, the mercury seals may be expelled. Therefore after sealing the tube, it should be handled only outside the seals, as otherwise the heat from the hands can easily expand the gas and expel the mercury. It is possible that extreme changes in temperature or barometric pressure from day to day may cause expulsion of the seals, though this has never occurred in the authors' laboratories.

The tube described above has several other important advantages. Simple rotation through an angle of 180° makes or breaks the seals; no shaking is needed as with other mercury-sealed tubes. The tube is inexpensively constructed and the simple design permits it to be made even by a relatively inexperienced glass blower. These are decided advantages, particularly when the tubes are to be used for class instruction where ease of operation is especially desirable and the breakage is likely to be great.

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# Colorimetric Microdetermination of Boron

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**R**ECOGNITION of the practical importance of boron in relation to agriculture is one of the recent interesting contributions of science. The failure to realize the full importance of boron earlier is due in part to the lack of a method of analysis sensitive enough to determine the small amounts usually present in soils or plants. Furthermore, the boron requirements of plants are confined to a narrow range of concentrations to avoid toxicity on one hand and deficiency of boron on the other. For crop plants in general, the concentration of soluble boron in soils should not exceed approximately one part per million of soil. A micromethod for the determination of boron in soils and plants is evidently desirable.

The early methods of analysis for boron were chiefly designed for macroamounts by separation and estimation by gravimetric or volumetric procedures (3, 5). Later, colorimetric methods for microamounts of boron were proposed (1, 2, 4, 6), but these methods were not satisfactory from the standpoint of rapidity or accuracy. Accordingly, this investigation was begun for the purpose of designing a method of analysis which would be sufficiently sensitive, accurate, and rapid for routine analysis of soluble boron in soils and in plants.

The need of a method for determining 1 to 10 micrograms of boron, and the desirability of employing small samples, 10 grams of soil or 1 gram of plant material, led to an investigation of colorimetric methods. The method proposed by Cassal and Gerrans (2) and the colorimetric method of Bertrand and Agulhon (1) offered sufficient promise in their sensitivity but seemed undesirable in the details of procedure and accuracy. The modification of the latter method proposed by Scott and Webb (6) is not entirely satisfactory, especially because it is necessary to employ extremely small final volumes of solution. Apparently, no further study has been made of the method of Cassal and Gerrans, which involves the distinctive use of oxalic acid instead of acetic acid in the boric acid-curcumin test, since it was reported in 1903. It was decided to follow the method of Cassal and Gerrans, in using colored solutions rather than test papers.

The method of Cassal and Gerrans is tedious and long. The solutions are evaporated to dryness several times; the volatilized boron is recovered in potash bulbs and finally added to the original boron not volatilized. It appeared that the above objection could be eliminated by utilizing certain steps in the method of Gooch (5) whereby solutions containing boron might be evaporated to dryness and the residue ignited without the loss of boron if an excess of calcium is present. Other details of the method investigated were concentration of reagents, time and temperature of drying residue, effect of volume, and method of measuring colored solutions.

## Method

The color reaction occurs when a solution of boric acid and oxalic acid is evaporated to dryness with curcumin; the solution is obtained when the dried residue is extracted with ethyl alcohol. An aliquot of the solution containing boron is rendered alkaline with calcium hydroxide, evaporated at full heat on the water bath, and then cooled to room temperature. Then oxalic acid and either curcumin or an extract of turmeric are added and evaporated to dryness at 55° C. and further heated at this temperature for 30 minutes. The

residue is taken up in 95 per cent ethyl alcohol, clarified by filtering or centrifuging, and compared with standards.

**REAGENTS REQUIRED.** A 0.10 *N* suspension of calcium hydroxide.

Solution containing 20 ml. of concentrated hydrochloric acid and 80 ml. of a saturated solution of oxalic acid prepared each day.

A 0.10 per cent curcumin or 1.0 per cent turmeric extract in 95 per cent ethyl alcohol. Shake occasionally for 4 to 6 hours and filter; this extract should be prepared daily.

Ethyl alcohol, 95 per cent.

Standard solution of boric acid.

## Procedure

Place an aliquot of a soil extract or plant ash extract, containing from 0.5 to 8.0 micrograms of boron in a porcelain evaporating dish. Render the extract alkaline by adding 5 ml. or more of a 0.10 *N* calcium hydroxide suspension and evaporate to dryness at full heat on a water bath. Remove the dish and allow to cool to room temperature, at the same time cooling the water bath to 55° ± 3° C. To the cooled residue add 1 ml. of the solution containing 80 ml. of a saturated solution of oxalic acid and 20 per cent hydrochloric acid, and 2 ml. of a 0.10 per cent extract of curcumin or 1 per cent turmeric. Rotate the dish so that the reagents come into contact with all the residue and evaporate to dryness on the water bath at 55° C. Continue heating for 30 minutes at this temperature, then remove the dishes and allow to cool.

Extract the residue with 95 per cent ethyl alcohol and transfer with a policeman to a filter or to a 15-ml. centrifuge tube. Filter and wash thoroughly with ethyl alcohol or throw down the solid phase with the centrifuge (about 10 minutes at 1500 r. p. m.) and dilute the liquid phase to constant volume; 25-ml. volume is convenient when using a 20-ml. cell with a colorimeter. Compare these solutions with standard solutions similarly prepared. The range of concentrations for the standards which have been used

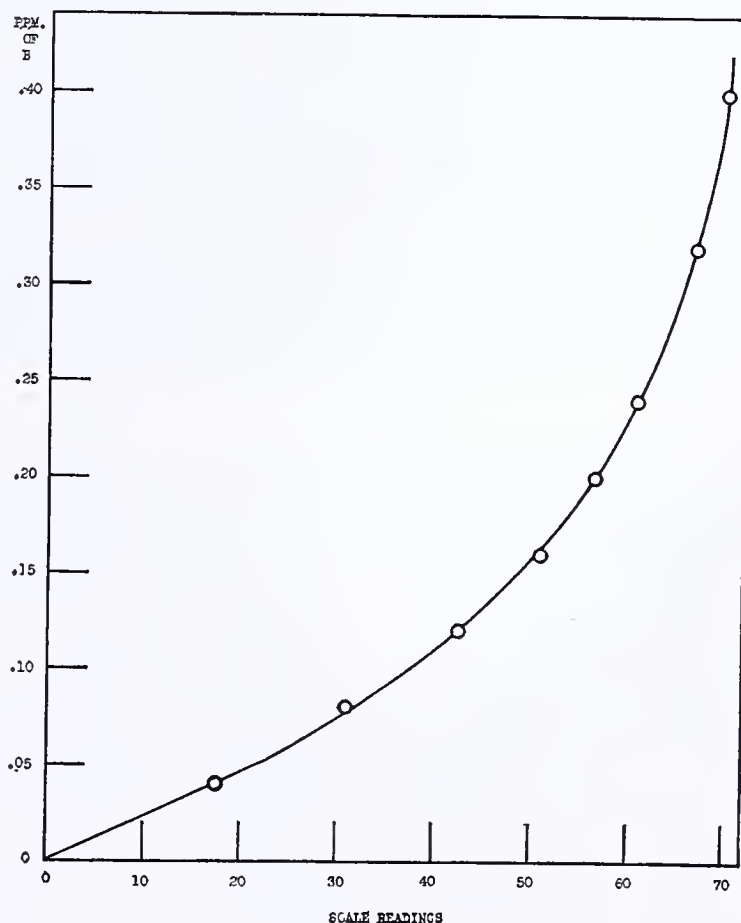


FIGURE 1. CALIBRATION CURVE OF BORON STANDARDS OBTAINED WITH ELECTROPHOTOMETER



TABLE I. EFFECT OF OXALIC ACID ON INTENSITY OF COLOR OF STANDARD BORON SOLUTIONS

Boron Solutions No.	P. p. m.	1 Ml. of Oxalic Acid of Different Concentrations			Increasing Amounts of 20 Per Cent Oxalic Acid		
		Per cent solution	Scale readings		Scale readings		ML.
1-2	0	5	0	0	1	0	..
3-4	0.04	5	5.8	5.0	1	18.7	..
5-6	0.04	10	15.8	15.0	2	16.9	16.9
7-8	0.04	20	18.8	17.8	3	15.4	13.0
9-10	0.04	40	19.5	18.7	..	..	..
11-12	0.16	5	21.2	20.0	1	52.1	..
13-14	0.16	10	40.0	38.0	2	49.5	52.5
15-16	0.16	20	48.4	48.2	3	45.7	48.0
17-18	0.32	5	31.2	37.5	1	64.0	..
19-20	0.32	10	49.0	28.0	2	66.0	66.1
21-22	0.32	20	65.6	64.0	3	61.3	60.0
23-24	0.32	40	66.8	65.0	..	..	..

TABLE II. EFFECT OF CURCUMIN AND TURMERIC ON INTENSITY OF COLOR OF STANDARD BORON SOLUTIONS

No.	Boron P. p. m.	0.10 Per Cent Curcumin			1.0 Per Cent Turmeric		
		Curcumin Scale readings	Scale readings		Turmeric Scale readings	Scale readings	
1-2	0	2.0	0	0	2.0	0	0
3-4	0.04	2.0	17.6	18.0	0.08	2.0	33.3
5-6	0.16	2.0	51.0	51.0	0.12	2.0	43.7
7-8	0.32	2.0	66.6	66.5	0.16	2.0	54.5
9-10	0	3.0	0	0.5	0.20	2.0	57.6
11-12	0.04	3.0	18.0	18.8	0	4.0	0
13-14	0.16	3.0	53.0	52.5	0.08	4.0	32.3
15-16	0.32	3.0	67.5	67.6	0.16	4.0	52.0
17-18	0	4.0	0	0	0.20	4.0	57.5
19-20	0.04	4.0	19.5	18.4	..	..	..
21-22	0.16	4.0	52.2	53.5	..	..	..
23-24	0.32	4.0	66.7	66.7	..	..	..

TABLE III. EFFECT OF DIFFERENT VOLUMES AT SAME CONCENTRATIONS ON INTENSITY OF COLOR OF STANDARD BORON SOLUTIONS

No.	Solutions		Scale Readings		Average
	Boron	Volume	Of duplicates		
	<i>P. p. m.</i>	<i>Ml.</i>			
1-2	0	25	0	0	0
3-4	0.10	25	40.3	39.0	39.65
5-6	0.20	25	56.9	58.7	57.80
7-8	0	50	0	..	0
9-10	0.10	50	39.2	40.4	39.80
11-12	0.20	50	59.0	59.8	59.40
13-14	0	100	0	..	0
15-16	0.10	100	38.2	38.0	38.10
17-18	0.20	100	56.3	54.7	55.50

is 0.02 to 0.32 p. p. m. of boron in a 25-ml. volume or 0.5 to 8.0 micrograms of boron diluted from a standard containing 1 p. p. m. of boron. A calibration curve for this range is shown graphically in Figure 1, as obtained with a Fisher electrophotometer.

Tests of Method

The proposed colorimetric micromethod for boron has been subjected to varied tests of changes in concentration of reagents as well as on different boron-containing substances. Representative results of some of these trials are given below.

OXALIC ACID REQUIRED. A standard solution of boric acid containing 1 p. p. m. of boron was analyzed with increasing amounts of oxalic acid. The results, shown in Table I, indicate that at least 1 ml. of a 20 per cent solution of oxalic acid is required while higher concentrations have little effect.

CURCUMIN OR TURMERIC EXTRACT REQUIRED. The standard solution of boric acid and blanks were analyzed with 2, 3, or 4 ml. of a 0.10 per cent solution of curcumin or with 2 and 4 ml. of a 1 per cent solution of turmeric. The results are shown in Table II. When the boron solutions containing different amounts of either curcumin or turmeric are read with their corresponding blanks the results are almost identical.

DIFFERENT VOLUMES AT SAME CONCENTRATIONS OF BORON. Two concentrations of a standard boron solution and blanks at volumes of 25, 50, and 100 ml. were analyzed to determine the effect of dilution on the results. As may be seen in Table III, there is little variation in the observed readings at the same concentration.

BORON IN SOIL EXTRACTS FROM GREENHOUSE SOIL CULTURES. In order to test the proposed method on soil extracts and to determine whether differences in soluble boron resulting from treatment in the greenhouse could be determined by the method, 10 grams of soil were extracted with 50 ml. of solution by three different methods. These results are summarized in Table IV. There were no difficulties encountered in the procedure, and with the exception of the two lowest amounts of boron in the extracts, satisfactory agreement between duplicate determinations was obtained.

BORON IN PLANT MATERIAL. Soybean hay from greenhouse liming experiments was analyzed by the proposed method for boron. Duplicate 1.0-gram samples of dried and ground plant material were ashed and dissolved with 1 cc. of N hydrochloric acid. The extracts were filtered, the residue was washed with hot water, and the filtrate was diluted to 50 ml. Duplicate aliquots of the ash extract were analyzed and the results are shown in Table V. Very satisfactory results were obtained by this procedure on plant material.

CONTAMINATION FROM ELEMENTS OTHER THAN BORON. In order to determine whether other elements would affect the method for boron, an aqueous extract from a fertile soil was added to known amounts of standard boron solutions. The solutions were analyzed and are reported in Table VI. The boron found in the soil extract and that in the standard solution are additive, and it appears that the ions other than boron did not contaminate the solutions as far as this method is concerned.

In the event that solutions containing excessive amounts of soluble salts are to be analyzed for boron and found to interfere with the determination, boron may be separated by volatilization with methyl alcohol in the usual way. The boron content may then be determined colorimetrically as outlined above.

TABLE IV. DETERMINATION OF SOLUBLE BORON

(Extracted by different methods from Ruston sandy loam obtained from greenhouse liming experiment)

Soil Treatment	Lime	Borax Lb./acre	Test No.	Boron Extracted		
				0.10 N HCl P. p. m.	Boiling water P. p. m.	Refluxing with water P. p. m.
None		0	1	0.090	0.120	0.888
			2	0.090	0.096	0.864
			Av.	0.090	0.108	0.876
150% Ca saturated		0	1	0.030	0.048	0.360
			2	0.060	0.072	0.420
			Av.	0.045	0.060	0.390
150% Ca saturated		15	1	0.300	0.336	1.280
			2	0.256	0.360	1.100
			Av.	0.278	0.332	1.190

TABLE V. BORON CONTENT OF SOYBEAN HAY (Grown in greenhouse with varying lime and borax treatments)

No.	Soil Treatment		Scale Readings		Boron in
	Lime, per cent Ca saturation	Borax Lb./acre			Dry Plants P. p. m.
1-2	50	0	34.7	33.5	10.5
3-4	150	0	24.5	24.5	7.0
5-6	150	0	24.0	23.8	
7-8	50	15	55.7	56.9	25.0
9-10	50	15	58.0	57.3	
11-12	150	15	70.8	70.3	50.0
13-14	150	15	71.9	71.9	
15-16	Blank	..	0	0	..



TABLE VI. EFFECT OF IONS OTHER THAN BORON ON DETERMINATION OF BORON

No.	Soil Extract <sup>a</sup> Ml.	Standard Boron Solutions		Boron Found P. p. m.	Total Boron Present P. p. m.	Error %
		Ml.	P. p. m.			
1-2	0	0	0	0	0	..
3-4	25	0	0	0.010	0.010	0
5-6	25	1.0	0.04	0.052	0.050	4.0
7-8	25	2.0	0.08	0.089	0.090	1.1
9-10	25	4.0	0.16	0.192	0.170	12.0
11-12	25	6.0	0.24	0.272	0.250	8.0
13-14	25	8.0	0.32	0.340	0.330	3.3

<sup>a</sup> 80.0 grams of Decatur clay extracted for 24 hours with 400 cc. of water.

### Discussion

The proposed method is most satisfactory when used with a photoelectric colorimeter in routine determinations. A calibration curve is readily formed from the readings obtained with a series of standards. From this curve, a table may be made to facilitate calculations of concentrations of boron in the samples. Obviously, the amount of curcumin or turmeric per unit volume must be kept identical with that of the blank; when this is done, dilutions of deeply colored solutions may be employed. Where a photoelectric colorimeter is not available, series of standards or balancing methods may be used but these methods require more time and are less accurate. The fact that the colors are reduced on standing after approximately 2 to 3 hours renders the series of standards method laborious unless artificial standards are used.

The substitution of 50 per cent ethyl alcohol, by volume, for the 95 per cent ethyl alcohol used for extracting the colored

residue gave satisfactory results when the solutions were read within an hour; on standing the aqueous extracts faded more rapidly than the alcohol extracts.

The substitution of 1 per cent turmeric extract for the 0.10 per cent curcumin is advisable, since the former is inexpensive and does not "crawl" in the evaporating dishes as much as the curcumin. These extracts deteriorate on standing in light and it is recommended that the extracts of turmeric be prepared daily.

All reagent flasks should be boron-free, since either acids or bases might extract boron from glass containing this element; Kavalier Bohemian glass is satisfactory. Calcium hydroxide was used to prevent the volatilization of boron and the 0.10 N suspensions served the purpose of obtaining a more intimate contact of the reacting substances at the drying point, the point at which the color is developed.

### Summary

A microgram procedure for a colorimetric microdetermination of boron involving the reaction between boric acid in the presence of oxalic acid and curcumin is outlined. It is accurate for the extremely low amounts of boron generally found in soil extracts and in plants.

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## Microviscometer

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**A microviscometer is described having absolute accuracy better than 4 per cent, and precision within 0.1 per cent in the range from 2 to 10,000 centistokes. The method is simple and rapid, and requires only one drop (about 0.03 gram) of sample.**

IN CONNECTION with some exhaustive fractionation of oils at this laboratory, a new viscometer has been developed. The instrument was designed primarily for examining extremely small samples, less than 0.1 gram, but is so simple, rapid, and accurate that it is believed to be as satisfactory in general viscometry as any of the popular macro types. The apparatus is entirely self-contained, and stands about 60 cm. (24 inches) high from a base 25 × 30 cm. (10 × 12 inches). While not intended for use as an absolute method, accuracy better than 4 per cent is obtainable in this sense; the precision is much closer, within 0.1 per cent. Even in the hands of an unskilled operator, the complete cycle of a determination, including sampling, charging, timing, and cleaning, requires less than 10 minutes.

The microviscometer discussed here is of the capillary type, but differs from the numerous modifications of the Ostwald pipet in that it has no bulb. Two such instruments have been described. That of Lidstone (2) depends in principle on the fall, under gravity, of a liquid column previously drawn up into the capillary from a small reservoir, the column being

continuous below the meniscus. The method is capable of good precision but is slow, because experimentally determined corrections must be made for surface tension and drainage. Levin's method (1) is rapid, but not capable of great accuracy. A short capillary dipping into a minute reservoir is again employed, but the transit of the meniscus rising with surface tension is timed. Many inherent errors exist in this method which cannot be easily corrected.

### Principle

The present method depends on the rate of fall, under gravity, of a short segment of liquid contained in a longer capillary. The tube is vertical, straight, and of uniform bore; a length of 25 cm. has been found convenient. It bears three etched marks, two near the bottom and one near the top, and is shown with its vapor jacket in Figure 1.

In making a determination, a minute drop of the liquid is placed on the open lower end of the tube, and, with the aid of suction, a column is drawn up to the first mark, C. The lower end is then wiped clean with filter paper or a lintless cloth, and suction again applied until the upper meniscus of the column segment is drawn above the top mark, A. Finally, the upper end of the capillary is opened to the air, and the transit of the upper meniscus between marks A and B is measured with a timing device.

### Theoretical Discussion

The classical law of Poiseuille for the flow,  $v$ , through a tube of radius  $r$  and length  $l$ , under a pressure  $p$  is as follows:



$$v = \frac{\pi p r^4}{8 l \eta} \quad (1)$$

where  $\eta$  is the viscosity of the fluid. Applied to the present problem, this reduces to the simple form.

$$k = \frac{g r^2}{8 L} t \quad (2)$$

where  $k$  is the kinematic viscosity,  $g$  is the acceleration of gravity, and  $L$  and  $t$  are the length and time of transit, respectively, of the meniscus between the two marks,  $A$  and  $B$ . Note that the length of the liquid column does not appear.

Poiseuille's law, however, is not strictly accurate for capillaries of finite length; corrections for end effects are required, and several well-known approximation formulas for these have been proposed. Experimentally, the magnitude of the error was determined by measuring the rate of fall of columns of different length, using the same liquid and tube. For the useful range of tube bores, this was found to be constant, or very nearly so, when the length of the segment was 100 or more times the diameter of the capillary. However, even though this error is very small, it is easily eliminated by fixing the length of the segment by the use of the third mark.

Surface tension introduces no error if the two menisci are identical. Primarily, this requires that they be of the same radius. This condition is fulfilled when the films of liquid on the walls of the capillary are of equal thickness before and behind the column. This state, in turn, is easily attained by drawing the column up at about the same rate at which it will later fall in making the test. The instruments must be equipped with vacuum-control bleed valves adjustable to give a head just twice that exerted by the column, so that the column is drawn up at the same rate as it will fall under gravity. Since the error is a secondary one, and oils never differ greatly in density, a fixed setting for the suction head has been found entirely satisfactory for such liquids.

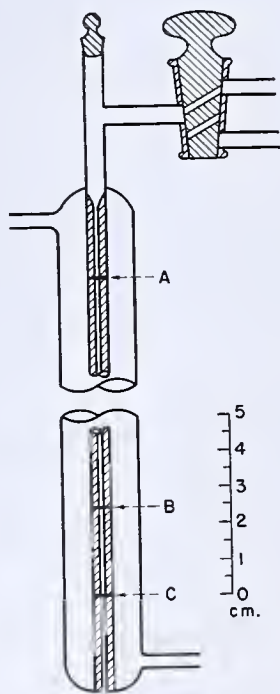


FIGURE 1

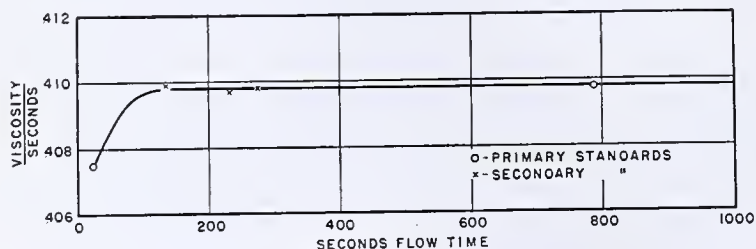


FIGURE 2. TYPICAL CALIBRATION CURVE

Flattening of the advancing (lower) meniscus, together with a corresponding increase in the curvature of the retreating one, is another possible source of error. Qualitative observation, however, under high magnification failed to show the effect. The tubes used are so small that the menisci appear to remain very nearly hemispherical at all times.

The viscosity of the air contained in the empty portions of the capillary introduces an error when the method is applied to liquids of very low viscosity, or when tubes of very small

bore are used. Calculation of the appropriate correction is simple.

### Calibration

Considering the basic principles discussed above, it is possible to use this type of viscometer as an absolute instrument. The following is a typical absolute calibration check run, using a highly refined petroleum lubricant of accurately known viscosity:

Bore of capillary, diameter, $\mu$	33.97
Distance, $A - B$ , cm.	15.0
Time, meniscus fall, $A - B$ , sec.	128.2
Kinematic viscosity, centistokes:	
Known	12.01
Observed	12.28
Error, %	2.2

The tube bore was determined by weighing mercury threads of measured length in it. Several such calibrations have been checked, using bores from 25 to 500  $\mu$ , and oils from 2 to 10,000 centistokes' viscosity.

The precision of this type of viscometer is far better than its absolute accuracy, however, and is apparently limited by the human element in timing at the low end of the range. Check runs can nearly always be made to agree within 0.1 per cent for reasonable flow times ( $>100$  seconds).

This being true, far better results can be obtained using the instrument as a relative one. A typical calibration curve is given in Figure 2. The primary standards are refined petroleum oils kindly supplied by M. R. Fenske, of Pennsylvania State College, and the secondary ones similar oils run against them in a FitzSimons viscometer.

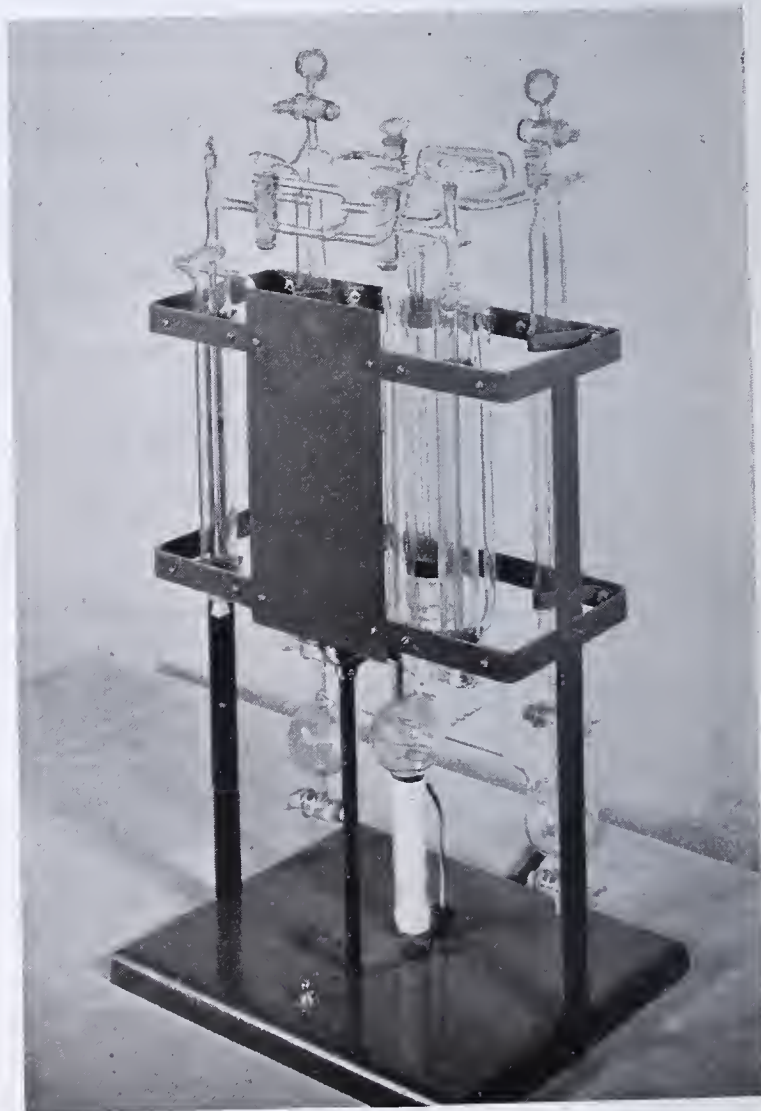


FIGURE 3. FRONT OF MICROVISCOMETER



## Description of the Instrument

Several viscometers of the present type have been built at this laboratory, and the form shown in Figures 3 and 4 has been found most satisfactory.

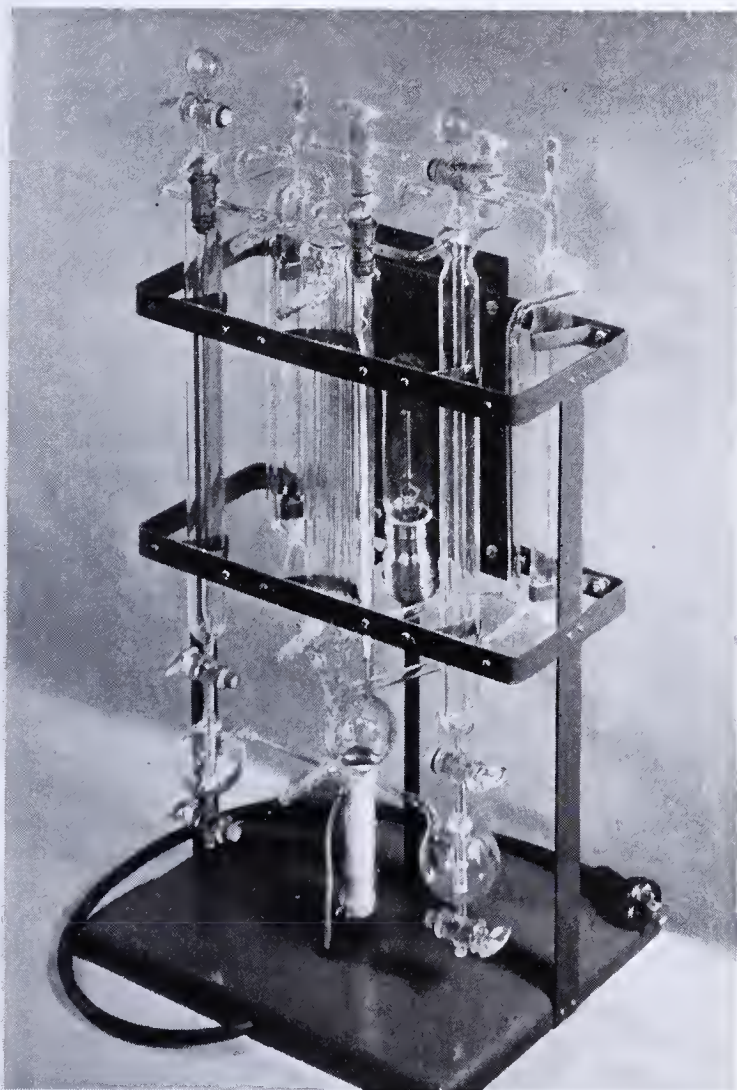


FIGURE 4. BACK OF MICROVISCOMETER

Two capillaries, of different bore, for different viscosity ranges, are jacketed and mounted at the front of the frame, near the sides. Between them is a small "showcase" lamp, protected by a metal plate shade, which also serves to truss the frame and support a calibration chart (not shown). Directly behind the lamp is a small boiler supplying vapor for temperature control, and a reflux condenser. The boiler heater is operated in parallel with the lamp from a small switch in the base.

Two vacuum controls are placed at the back corners of the frame. One, using *s*-tetrabromoethane, regulates the pressure at the top of the condenser, and hence the capillary temperature. Temperatures are read on an A. S. T. M. Saybolt thermometer hanging with its bulb above the liquid in the boiler. For Pittsburgh's elevation, methylene chloride, acetone, and diisobutylene are satisfactory for temperatures of 37.78°, 54.44°, and 98.89° C. (100°, 130°, and 210° F.), respectively. The other bubbler, filled with kerosene, controls the suction used to draw the sample into the capillary. For precise work, it should be adjusted according to the density of the unknown, but for petroleum products a mean fixed setting has been found satisfactory. Both adjustments are readily made with a valveless rubber atomizer bulb communicating with the reservoirs.

The apparatus is assembled with glass seals throughout.

The model described is easily portable and entirely self-contained. Connections are required to a 110-volt electric line (power demand about 100 watts), vacuum, cold water, and drain. Although the glass part is complex, it is so compact and well protected by the frame that the unit is very rugged. Two such

complete instruments have been in use at this laboratory for general routine work for nearly 3 years without difficulty.

Temporary improvised viscometers of this type have been made from broken thermometer stems. Two stoppers and a large glass tube form the jacket, used as a water bath. An ordinary -10° to 110° C. thermometer capillary was found to give very nearly Saybolt seconds as flow time for the more viscous oils when the *A-B* distance was 8.9 cm. An all-glass, vapor-bath type, however, is recommended if many determinations are to be made.

## Procedure

The operation of the viscometer is so simple that detailed description is scarcely necessary.

First the boiler is started. After steady operation has been obtained, as indicated in the condenser, the temperature is adjusted with the right-hand vacuum control. Response is complete within a few seconds, and seldom more than two or three trials are necessary to set the temperature to within 0.01° C. (0.02° F.) of that desired. Occasional small readjustments are sometimes needed to follow the changes in barometric pressure through the day.

The left-hand control should be set so that its head of kerosene is equal to twice the head of the sample column, but a fixed setting may be used for most oils. This adjustment is not critical.

The liquid is best applied to the capillary with a small wire loop, similar to those used in blowpipe bead tests. After the drop is in place, suction is applied to the tube by opening the appropriate three-way stopcock at top front. As the sample rises, a filter paper or lintless cloth is held in readiness to wipe the end clean. This may be done in several ways. With a little practice, an operator can learn to break the column without interrupting the suction just as the meniscus passes the first mark. A slower method, perhaps better, especially for light oils, consists in drawing the column up slightly beyond mark *C*, turning the stopcock to open the upper end of the tube to the air, and simultaneously pressing the wiper squarely and firmly against the lower end of the tube. The meniscus will then fall slowly, as the liquid is absorbed in the wiper, and may easily be caught exactly at the mark by turning the stopcock back to the vacuum side, which will cause the column to break sharply at the lower end of the capillary.

The liquid segment is now allowed to rise above *A*, the upper end of the tube is opened to the air by means of the stopcock, and the time required for the upper meniscus to pass from that mark to *B* is recorded. No waiting is necessary, since the liquid comes to temperature almost instantly. Alternatively, to obtain a shorter flow time for heavy samples using the same pipet, the liquid is raised so that its lower meniscus is just above mark *B*, and its time of fall from that point to *C* is observed. In this way a two-capillary unit may have four ranges. Choice of proper range is important; flow times should be kept between 100 and 1000 seconds, the first limit for accuracy, the second for convenience.

Check runs may be made, after a test has been completed, using the same sample column.

For cleaning the capillary, 2 or 3 drops of volatile solvent are poured into it by removing the tiny ground stopper at the top of the apparatus, and wiping the solvent off at the lower end as it comes through. If the solvent used boils just a few degrees above the working temperature, the tube may be dried in a few seconds by suction. An occasional thorough cleaning (once a month during continuous operation) with dichromate-sulfuric acid solution is recommended.

## Acknowledgments

The writer is indebted to S. Frederick Kapff for some of the work of calibration of the instruments, and for many of the details of the procedure, and to William E. Barr, of the Gulf Research and Development Company, for his skillful and patient glass working.

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# Quantitative Organic Elementary Microanalysis without a Microbalance

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The standard micromethods of quantitative organic elementary analysis allow a wide range in the amount of sample used, from about 1 mg. as the minimum to about 20 mg. as the maximum. The amount of sample to be taken for analysis depends upon the sensitivity and the precision of the balance employed. This relationship has now been established.

Not only can microbalances of less than standard sensitivity and precision be used,

but an assay or even an ordinary analytical balance can be substituted for the standard microbalance, if its sensitivity and precision are not less than 0.025 mg. Minor changes in some of the microprocedures, but no changes in the standard microapparatus and equipment are necessary. Thus the lack of a microbalance need no longer delay the adoption of standard quantitative organic microchemical methods in teaching as well as in actual industrial practice.

FROM the very beginning of quantitative organic microanalysis the necessity of employing a microbalance has prevented the rapid spreading and universal adoption of standard microchemical methods in this field.

There are several possible ways to eliminate the use of a microbalance. One possibility consists in changing the standard microchemical procedures as little as possible, using an assay or an ordinary analytical balance of high sensitivity, and increasing the amount of sample accordingly. This was successfully done by Pregl (7) in his very first microchemical determinations, by Wise (13) for the early Pregl microdetermination of carbon and hydrogen, and by Schmitt (9) for the vaporimetric microdetermination of molecular weight. Another possibility is to employ a regular analytical balance, showing the usual sensitivity of 0.1 mg., and to dilute the sample either with an inert solvent (6) or with the reagent (8). Still another possibility is to use the same type of balance and to discard the standard micromethods altogether and devise independent semimacro-, semimicro-, or meso-micromethods (2, 3, 10-12).

The correlation of the precision of a given analytical balance with the general mathematical postulations governing the replacing of a microbalance of standard precision by a balance of lower precision, as given by Benedetti-Pichler (1), made it possible to calculate beforehand the minimum amount of sample to be taken for a given determination. These postulations provided the basis for the systematic extension of the work of previous investigators (7, 9, 13) to the entire field of organic microanalysis. Barring extreme cases [ $s > r$ ;  $s$  = weight of sample;  $r$  = weight of reaction product (1)], rigid application of these mathematical postulations is not necessary for practical purposes. It is enough to determine the sensitivity and precision of a given balance and calculate the minimum amount of substance required to give weighing results within the limits of error of the micromethod in question.

For general practice it appears advisable to adhere to the limits shown in Table I for the amount of sample to be taken for analysis.

A regular analytical balance showing a sensitivity and a precision of 0.022 mg., both determined as described below, was selected for use, instead of a standard microbalance, in teaching the fundamental methods in quantitative organic

microanalysis. The procedures as described by Niederl and Niederl (4) were followed. It was found that with a balance of the sensitivity and precision of 0.022 mg., no changes whatsoever were necessary in the standard apparatus and equipment. The procedures also remained unchanged, with the exception of the time factor in some of the determinations (carbon and hydrogen; Dumas nitrogen).

The results given below were obtained by several graduate students taking the regular course in quantitative organic microanalysis, and using the same equipment and apparatus as employed by the students assigned to standard microbalances. The results were not selected, nor were any omitted. They are given in the order actually obtained and include the very first analyses.

The terms "micromethod", "microanalysis", or "micro-procedure" are used in accordance with the definition given in INDUSTRIAL AND ENGINEERING CHEMISTRY [Anal. Ed., 11, 111 (1939)].

TABLE I. LIMITS OF SAMPLE

Precision of Balance Mg.	Amount of Sample Theoretical minimum Mg.	Practical average Mg.
0.001	0.3 <sup>a</sup> -0.4 <sup>b</sup>	3-5
0.002	0.6-0.8	4-6
0.005	1.5-2.0	5-8
0.010	3.0-4.0	6-10
0.020	6.0-8.0	8-12

<sup>a</sup>  $s < r$ .    <sup>b</sup>  $s = r$ .

## The Balance

The balance used in the determinations described herein was selected from a number of student balances available at this college in the laboratory for quantitative inorganic analysis. In order to perform the weighings in exactly the same manner as with a standard microbalance, the milligram markings on the beam were designated to be read as follows: The original 5-mg. mark at the extreme left was regarded as the new zero mark; consequently the original zero mark became the new 5-mg. mark and the original 5-mg. mark at the extreme right became the new 10-mg. mark. The subdivisions, the 0.1-mg. marks, were ignored. The balance was set up alongside the standard Kuhlmann microbalances in the same room. A 5-mg. rider was employed.

ADJUSTMENT AND DETERMINATION OF ZERO READING. The screws on the horizontal beam were then set so that the balance



TABLE II. SENSITIVITY OF BALANCE

	Position of Rider on the Rider Scale Mg.	Deflection Sum on Pointer Scale, Reading Units	Sensitivity of Balance, Pointer Scale Reading Units
No load	0	0	47 <sup>a</sup>
	1	-47 (4.7 divisions)	
10-gram load	0	-10 (1 division)	
	1	-35 (3.5 divisions)	45 <sup>b</sup>

<sup>a</sup> 1 unit on pointer scale equals 0.021 mg.<sup>b</sup> 1 unit on pointer scale equals 0.022 mg.

gave a zero reading when the rider rested on the new zero mark on the rider scale (4, p. 15). The zero readings themselves gave extremely constant values and no corrections were necessary.

**DETERMINATION OF SENSITIVITY** (4, p. 16). The sensitivity of the balance was determined with and without a load. The results given in Table II were obtained. Thus one division on the pointer scale corresponds to 0.220 mg. and one tenth of such a division, the "reading unit" in microchemical weighings, to 0.022 mg. (22 micrograms).

**DETERMINATION OF PRECISION.** The precision of the balance (4, pp. 17-18) with a 10-gram load on both weighing pans, was determined by two series of weighings, performed during a period of 2 hours. After each weighing the rider was raised and placed as exactly as possible on the same mark. The weights on the pans were lifted and put back again as close to the original position as possible (Method A). Then a second series of weighings was carried out in which the weights on the pans were always placed considerably off the center of the weighing pans (Method B). The results (average deviations) were as follows:

	Pointer Scale Readings	Divisions	Mg.
Method A, 14 weighings	0.7	0.07	0.015
Method B, 12 weighings	1.2	0.12	0.026
Average, 26 weighings	1.0	0.10	0.022

Since during the actual weighing the distribution of mass on the balance pans will sometimes follow that of the first series and sometimes that of the second, all figures obtained were averaged and the practical precision of the balance under these conditions was calculated as shown above. This indicates that weighings on this balance can be duplicated within  $\pm 0.022$  mg. (22 micrograms).

The practical weighings were carried out according to the method of weighing on a microbalance (4, pp. 14-21). Thus each division on the pointer scale was mentally divided into 10 units. The rider was moved whole milligram divisions on the rider scale, and the milligram fraction was obtained by multiplying the deflection sum on the pointer scale by 0.022.

### Determination of Metals

The first procedure was the determination of the percentage of metal in metallo-organic salts (4, pp. 41-3).

TABLE III. DETERMINATION OF METALS

Substance	Weight of Substance	Weight of Residue	Metal		
	Mg.	Mg.	Found %	Calcd. %	Error %
Potassium bitartrate	11.31	5.20	20.63	20.79	-0.16
	11.58	5.32	20.61		-0.18
	10.82	4.91	20.36		-0.43
Sodium oxalate	9.63	10.24	34.43	34.33	+0.10
	9.04	9.63	34.49		+0.16

### Determination of Neutralization Equivalent

The second procedure was the standardization of the 0.01 *N* sodium hydroxide solution by means of benzoic acid, and then the determination of the neutralization equivalents of cinnamic and salicylic acids (4, pp. 44-50; 5). In this method the weight of material taken is limited by the capacity of the microburet, which is 10 ml.

TABLE IV. DETERMINATION OF NEUTRALIZATION EQUIVALENT

	Weight of Acid Mg.	0.01 <i>N</i> NaOH Ml.	Factor <sup>a</sup>		
	12.42	9.57	1.063		
	10.23	7.91	1.059		
Substance	Weight of Acid Mg.	0.01061 <i>N</i> NaOH Ml.	Neutralization Equivalent		
			Found	Calcd.	Error
Cinnamic acid	12.00	7.77	146	148	-2.0
	12.13	7.82	146		-2.0
Salicylic acid	13.78	9.54	136	138	-2.0
	12.55	8.54	139		-1.0

<sup>a</sup>  $N = F \times 0.01$ . Found by dividing theoretical number of ml. of 0.01 *N* alkali required by sample, by number of ml. actually consumed in neutralization. There are two separate factors, one for phenolphthalein and another for methyl red (4, p. 47; 5).

### Volumetric Determination of Aminoid Nitrogen

In the determination of aminoid nitrogen by the Kjeldahl method (4, pp. 51-8; 5), the precaution observed was to take a small enough sample so that no more than 10 ml.—the capacity of the buret—of standard 0.01 *N* acid is required.

TABLE V. DETERMINATION OF AMINOID NITROGEN

Substance	Weight of Sample Mg.	0.00998 <i>N</i> HK(IO <sub>3</sub> ) <sub>2</sub> Ml.	0.01068 <i>N</i> NaOH Ml.	Nitrogen		
				Found %	Calcd. %	Error %
<i>p</i> -Toluamide	8.46	9.44	2.96	10.37	10.37	-0.00
	8.35	9.21	2.75	10.49		+0.12
Myristamide	9.07	9.41	5.17	5.98	6.17	-0.19
	7.96	8.63	4.82	6.04		-0.13
	9.53	9.13	4.67	6.06		-0.11

### Gasometric Determination of Nitrogen (Table VI)

The next procedure tested was the gasometric determination of nitrogen by the Dumas method (4, pp. 60-78). After several attempts it was found that to obtain satisfactory analyses the speed of the gas bubbles throughout the entire period of analysis had to be reduced to one bubble per second. Consequently the time of the first and the second combustion, as well as the washing out process (4, pp. 72-3), had to be doubled. Thus the entire analysis required about 2 hours. It was also found advisable to double the amount of fine copper oxide in the mixing procedure (4, p. 70).

### Determination of Carbon and Hydrogen

The carbon and hydrogen determination (4, pp. 80-115) required several changes before satisfactory analyses were obtained. The combustion was carried out at such a rate that the substance distilled or vaporized slowly and evenly into the filling of the combustion tube. This was brought about as follows:

The boat was placed 7 to 8 cm. instead of 5 cm. in front of the combustion tube filling, and the furnace was kept at a temperature of from 700° to 750° C. The heating was started as usual 5 cm. in front of the boat, and the boat was approached by the flame at the usual rate till the substance started to distill or decompose. The burner was halted at this point till all the material distilled out of the boat. Then the burner was slowly advanced till it was directly under the boat, and was kept there until the material had distilled into the combustion tube filling in the furnace.



TABLE VI. GASOMETRIC DETERMINATION OF NITROGEN

Substance	Weight of Sample Mg.	Vol. of N <sub>2</sub> , Corrected Ml.	Pres- sure Mm.	Temp. ° C.	Nitrogen—		
					Found %	Calcd. %	Error %
Azobenzene	8.66	1.155	754	26	15.11	15.38	-0.27 <sup>a</sup>
	8.44	1.109	753	30	14.67		-0.71 <sup>a</sup>
	7.37	0.999	758	26	15.44		+0.06
	7.51	1.024	758	26	15.53		+0.15
	8.02	1.082	757	26	15.34		-0.04
2,4-Dinitrobenzoic acid	9.48	1.077	765	24	13.14	13.21	-0.07
	8.93	1.056	764	31	13.34		+0.13
Research Substances							
C <sub>10</sub> H <sub>12</sub> O <sub>2</sub> NSCl	9.13	0.468	764	31	5.78	5.72	+0.06
C <sub>20</sub> H <sub>21</sub> NO <sub>2</sub>	12.07	0.460	762	22.5	4.42	4.56	-0.14
	8.85	0.347	761	23	4.53		-0.03
C <sub>12</sub> H <sub>16</sub> ONSCl	7.98	0.374	764	29	5.33	5.43	-0.10

<sup>a</sup> These two analyses were performed before proper duration of period of combustion had been determined.

If at any time during the combustion the rate of flow of the water from the Mariotte flask decreased because of choking of the capillary by water, the burner was halted until the pressure had returned to normal. This precaution was particularly necessary for substances which distilled rather than decomposed. By this procedure the first combustion period was increased from 15 to 25 minutes. After the substance had vaporized, as observed by the disappearance of the distillate, the gas burner was advanced as usual. During both the combustion and sweeping out period, with the latter extended to 30 minutes, the capillary end of the combustion tube and the constrictions of the water-absorption tube required mechanical heating with a heated file to drive over the water which tended to deposit in the capillary (total time, 60 minutes; 300 ml. of oxygen).

TABLE VII. DETERMINATION OF CARBON AND HYDROGEN

Substance	Weight of Sample Mg.	Weight of CO <sub>2</sub> Mg.	Weight of H <sub>2</sub> O Mg.	Carbon—			Hydrogen—		
				Found %	Calcd. %	Error %	Found %	Calcd. %	Error %
Sulfonal	9.66	12.85	5.80	36.28	36.79	-0.51	6.72	7.09	-0.37
	10.11	13.42	6.15	36.20		-0.59	6.84		-0.25
d-Glucose	9.13	13.56	5.46	40.50	40.00	+0.50	6.67	6.69	-0.02
	10.08	14.78	5.85	40.01		+0.01	6.52		-0.17
	9.78	14.26	5.54	39.80		-0.20	6.34		-0.35
Resorcinol	10.80	25.89	4.80	65.38	65.45	-0.07	5.00	5.45	-0.45
	9.96	23.65	4.36	64.79		-0.65	4.90		-0.55
	12.94	31.15	6.39	65.66		+0.21	5.53		+0.08
Benzoic acid	10.26	25.67	4.54	68.30	68.88	-0.58	4.94	4.92	+0.02
	9.82	24.85	4.11	68.99		+0.11	4.68		-0.24
	11.89	30.15	5.29	69.15		+0.27	5.00		+0.08
Naphthalene	10.41	35.82	5.96	93.84	93.75	+0.09	6.40	6.25	+0.15
	10.70	36.61	5.98	93.34		-0.41	6.25		-0.00
Research Substances									
C <sub>13</sub> H <sub>23</sub> BrO <sub>3</sub>	10.16	21.74	5.89	58.39	58.42	-0.03	6.48	6.56	-0.08
	12.22	26.20	6.37	58.47		+0.05	5.84		-0.72
C <sub>20</sub> H <sub>23</sub> O <sub>4</sub>	10.79	28.51	8.31	72.06	72.29	-0.23	8.61	8.43	+0.17
	10.40	27.42	8.16	71.96		-0.33	8.78		+0.35
C <sub>15</sub> H <sub>15</sub> O <sub>6</sub>	9.96	25.63	4.70	70.18	69.93	+0.25	5.28	5.52	-0.24
C <sub>21</sub> H <sub>26</sub> O <sub>2</sub>	8.24	22.29	5.40	73.78	73.68	+0.10	7.33	7.62	-0.29
C <sub>17</sub> H <sub>24</sub> Br <sub>2</sub> O <sub>2</sub>	8.82	15.78	4.52	48.77	48.57	+0.20	5.73	5.71	+0.02

### Determination of Molecular Weight (Table VIII)

The cryoscopic method (4, pp. 171-4) had to be slightly modified as follows:

A melting point tube was used having an inside diameter of 3 mm. at the base instead of the usual 2 mm., in order to facilitate mixing of the substance with the greater amount of camphor; the thickness of the walls of the tube was increased because of the increase of the internal pressure.

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TABLE VIII. DETERMINATION OF MOLECULAR WEIGHT

Substance	Weight of Sample Mg.	Weight of Camphor Mg.	Δ	Molecular Weight—		
				Found	Calcd.	Error
Resorcinol	2.37	21.65	39.9	109.7	110.2	-0.5
	1.66	24.52	24.1	112.4		+2.2
Azobenzene	2.39	22.63	23.3	181.8	182.2	-0.4
	2.36	22.18	23.2	183.6		+1.4
Naphthalene	2.93	21.53	42.2	129.1	128.0	+1.1

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# INDUSTRIAL and ENGINEERING CHEMISTRY

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## Multiple Tests on Catalysts for Coal Hydrogenation

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IN THIS paper a simple method of experimental liquid-phase hydrogenation is described, and its application to the testing of catalysts for coal liquefaction is illustrated.

The method consists essentially in heating a number of separate samples of coal or other material in a stream of hydrogen under pressure. The loss in weight during this treatment is a measure of the amount of distillable products, which increases as the conditions of hydrogenation are improved. The principal advantage of the method over those now in use is that it is a relatively quick and inexpensive means of studying the effects of variations in the material charged. However, it has the disadvantage that the properties of the volatile products cannot be determined. Its proper use, therefore, is for the preliminary investigation of such subjects as catalysis, which require extensive experimentation.

### Apparatus

The apparatus, as used at the Fuel Research Laboratories of the Canadian Bureau of Mines, is illustrated in Figures 1 and 2.

The dishes containing the samples are of Pyrex glass, and can be easily made from tubing of about 2.5-cm. diameter. Under the conditions of the tests reported herein, there is no significant change in the shape or weight of the glass—for example, the weights of two dishes exposed during a test at 445° C. and 204 atmospheres (3000 pounds per square inch) for 5 hours were as follows:

	No. 6	No. 20
Weight of dish, grams:		
Before hydrogenation	2.5315	2.5576
After hydrogenation	2.5316	2.5579

In the reaction chamber, the dishes are spaced at intervals of 1.8 cm. in a vertical column. Variation of the distance between them does not affect the results, as is shown by the following pairs of comparable tests:

Test No.	Space above Dish, Cm.	Loss in Weight, Per Cent of Ash- and Moisture-Free Coal
1-3	2.7	52.1
1-4	5.4	51.7
1-9	2.7	57.5
1-10	5.4	58.0
2-10	1.8	56.2
2-12	3.5	55.1
2-30	1.8	55.7
2-32	3.5	56.5

The number of dishes in the column is limited to about fifty by the difficulty of maintaining a constant temperature over a

long section of the reaction chamber. The temperatures are measured at the top, center, and bottom of the column by three thermocouples, located inside the tube to which the dishes are attached, and recorded automatically.

The reaction chamber, and also the auxiliary equipment used for heating it and for compressing and recirculating hydrogen, have been described previously (5).

### Procedure

When a catalyst is to be used, it is weighed into a bottle in the form of a powder, and the corresponding quantity of pulverized coal is added. The bottle is shaken for 5 minutes to mix the coal and catalyst. The degree of mixing is not an important factor, for the results after shaking for 5 seconds and for 1 minute were practically identical. When a concentration of catalyst of the order of 0.01 per cent is to be made up, it is more convenient to add coal to a mixture having a concentration about ten times higher than to handle the minute amount of catalyst required. With this exception, it is best to make up the samples in order of increasing concentration in order to minimize the possibility of contaminating a dilute mixture with a concentrated one.

The rank of the coal has a major influence on the yield of volatile products and on the efficiency of catalysts. The particle size of the coal also has an effect. However, throughout the present work, only one batch of pulverized coal has been used, so that allowance need not be made for these factors.

The quantity of coal in the sample has a minor influence on the yield of volatile products. As might be expected, the smaller quantities give higher yields. In a series of tests on this variable, the loss in weight increased progressively from 57 to 62 per cent, when the weight of coal per sample was decreased between 1.0 and 0.2 gram. Throughout the catalyst tests, the samples have weighed between 0.6 and 0.9 gram.

When a vehicle is used, it is added after the sample of coal and catalyst has been weighed into the glass dish. The vehicle is measured from a 1-ml. pipet and is not weighed. Since the vehicle used in the present tests is a distillate product, practically all of it evaporates at the temperature of the reaction. Its influence, therefore, may not be the same as that of vehicles employed in a comparatively small closed system, where a considerable volume of vehicle remains in the liquid phase throughout the test.

After the samples have been weighed into the dishes and the vehicle, if any, has been added, the dishes are placed in the holders and the column is lowered into the reaction chamber. The head of the reaction chamber is tightened, and hydrogen is admitted slowly to avoid disturbing the pulverized coal. The heaters are then turned on, and the temperature is brought to about 445° C. in 2 hours. During the latter part of the heating period, the temperature rises at the rate of 3° C. per minute. During the heating period, the pressure in the system is brought up to 204 atmospheres (3000 pounds per square inch). When the temperature has reached 445° C., a flow of hydrogen at the rate of about 110 liters per hour at the conditions of the reaction, or 0.8 linear cm. per second in the unobstructed part of the reaction chamber, is begun. These conditions—445° C., 204 atmospheres,



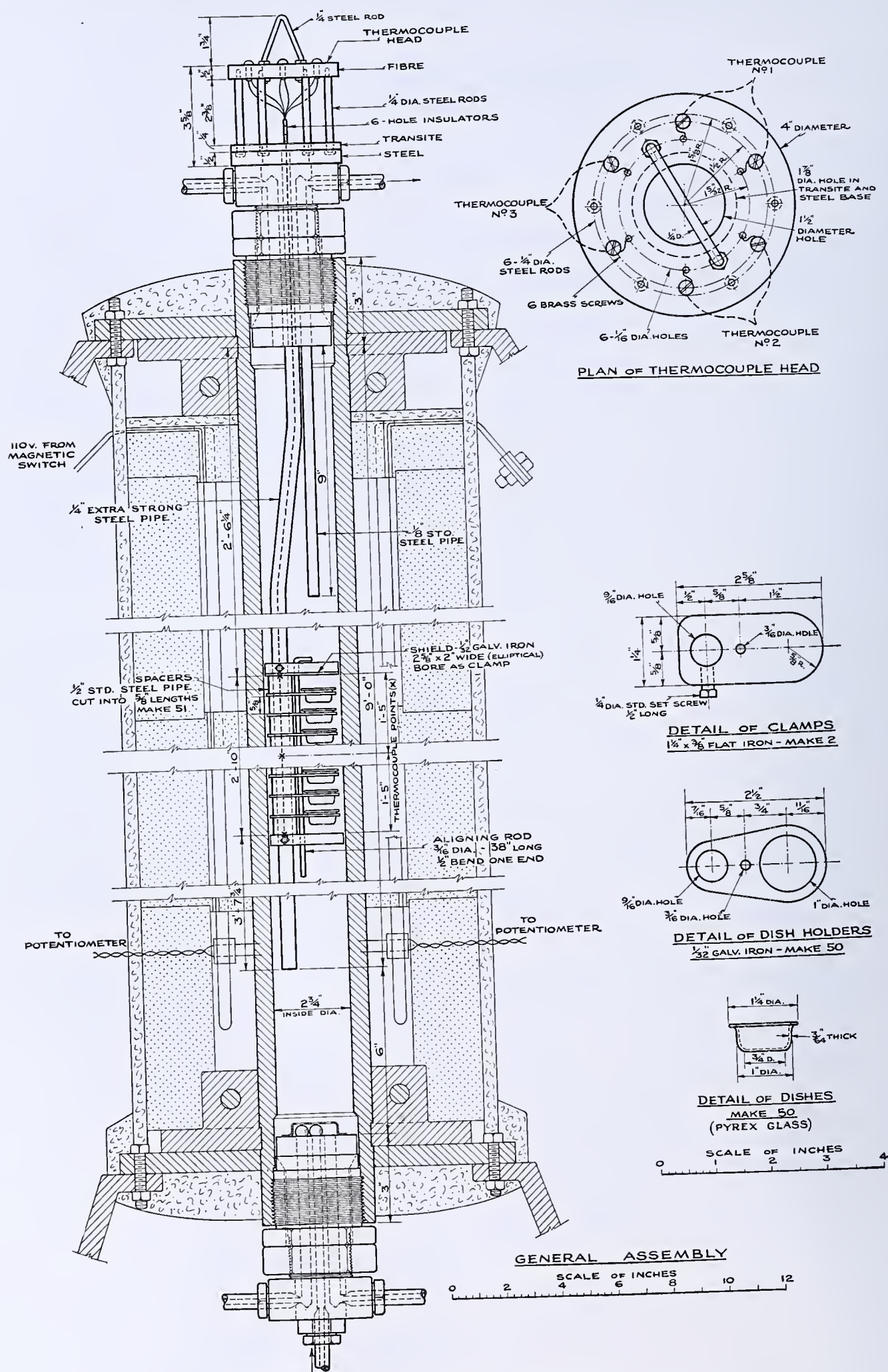


FIGURE 1. APPARATUS FOR MULTIPLE HYDROGENATION TESTS



TABLE I. PROXIMATE AND ULTIMATE ANALYSES

	As Used in Tests	Ash- and Moisture- Free Basis
Proximate analysis, %:		
Moisture	2.1	..
Ash	3.3	
Volatile matter	37.2	39.3
Fixed carbon	57.4	60.7
Ultimate analysis, %:		
Carbon	79.7	84.2
Hydrogen	5.7	5.8
Ash	3.3	
Sulfur	1.0	1.1
Nitrogen	1.7	1.8
Oxygen	8.6	7.1
Calorific value, calories per gram, gross	7960	8420

TABLE II. ANALYSIS OF ASH

	Per Cent of Ash	Per Cent of Coal
Ignition loss at 700° C.	2.29	0.076
SiO <sub>2</sub>	25.76	0.850
Al <sub>2</sub> O <sub>3</sub>	17.72	0.585
Fe <sub>2</sub> O <sub>3</sub>	35.44	1.170
TiO <sub>2</sub>	0.86	0.028
CaO	6.65	0.219
MgO	0.94	0.031
Na <sub>2</sub> O	4.09	0.135
K <sub>2</sub> O	0.49	0.016
SO <sub>3</sub>	4.77	0.157
MnO	0.20	0.007
P <sub>2</sub> O <sub>5</sub>	0.44	0.015
Total	99.65	3.289

TABLE III. SIEVE ANALYSIS  
(U. S. standard sieve)

	%
On 50-mesh	6.0
Through 50-, on 100-mesh	14.2
Through 100-, on 140-mesh	14.7
Through 140-, on 200-mesh	17.9
Through 200-, on 300-mesh	11.2
Through 300-mesh	36.0

and a rate of flow of about 0.8 cm. per second—are maintained for a period of 5 hours, after which the heating current is shut off and the chamber allowed to cool.

After the chamber has cooled, the dishes containing the residues are removed and weighed. The loss in weight is corrected for the loss from the catalyst and for the moisture in the original coal. The yield of volatile material is taken as the corrected loss in weight calculated as per cent of the ash- and moisture-free coal. The loss from the catalyst is determined by treating a sample of the catalyst alone under the conditions of the test. This, of course, implies the assumption that the catalysts react in the same way in the presence and absence of coal, which, in some instances, is probably incorrect. However, this correction is usually so small that no large error is involved.

The reaction is sensitive to small changes in temperature. Thus, the average yield of twelve samples, treated at an average temperature of 443° C. was 58.3 per cent, and that of twelve samples, similarly treated at 445° C., was 56.1 per cent. Since there are unavoidable variations in temperature over the length of the column, inaccuracies as great as 3 per cent are possible in comparing samples located at different positions. As a correction, duplicate samples of coal containing no catalyst are located at six equidistant points on the column in each multiple test, and a graph is constructed of their loss in weight *vs.* their position. Each experimental sample is compared with the value on the graph corresponding to its position in the column. The measure of the efficiency of a catalyst is taken as the difference between the yield obtained with it and that which would have been obtained in the same position in its absence as read from the graph. The yield of volatile products from the coal used for the present tests was about 57 per cent in the absence of any catalyst, and more than 80 per cent in the presence of the more efficient catalysts.

Tests on Catalysts

The coal used throughout the tests on catalysts was produced in the Sydney area in Nova Scotia. Its rank was high-volatile A bituminous in the classification of the American Society for Testing Materials. The characteristics of the coal and its ash are given in Tables I, II, and III.

The vehicle added to some of the samples was representative of those which had been employed in the continuous tests at these laboratories. It was a part of the product of hydrogenation of a high-volatile A bituminous coal, produced by distilling the product to coke with open steam and discarding a low-boiling fraction. The distillation range, determined in the Hempel apparatus, was as follows:

Fraction	Per Cent by Weight
Water	0.2
Up to 170° C.	0.4
170 to 230° C.	12.8
230 to 300° C.	37.6
Above 300° C.	48.9
Distillation loss	0.1

Although this vehicle was entirely a distillate, it contained 0.003 per cent of tin. The increase in the yield of volatile products due to its use is as follows:

Test No.	Increased Yield, Per Cent of Ash- and Moisture-Free Coal
3-3	8.6
3-4	9.5
Av.	9.1

Before beginning a survey for the purpose of testing the catalytic activity of a large number of materials, it was thought advisable to study a few known catalysts in different concentrations, and in the presence and absence of a vehicle. This was done partly to establish standard conditions for the tests, and partly to observe and compare the behavior of the known catalysts over a wide range of concentration. The catalytic materials were not specially prepared, but were used as received from the chemical supply houses.

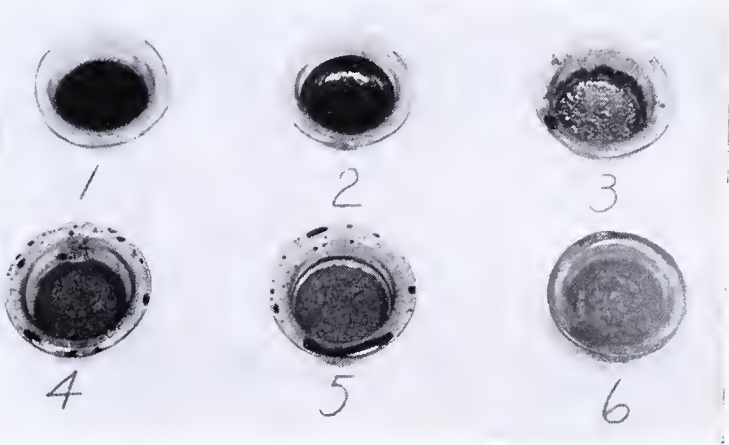


FIGURE 2. SAMPLE DISHES

- 1. Coal as charged
- 2. Residue from coal only
- 3. Residue from coal plus vehicle
- 4. Residue from coal plus vehicle plus 5 per cent stannous oxalate
- 5. Residue from coal plus vehicle plus 5 per cent stannous oxide
- 6. Residue from coal plus vehicle plus 9 per cent ammonium molybdate

STANNOUS OXIDE. Stannous oxide has been used in nearly all the continuous tests at these laboratories, and has also been used extensively as stannous hydroxide by the (British) Fuel Research Board (2). Its efficiency, under a variety of experimental conditions, was therefore known and it was well suited for the present work. The sample used for these tests had been prepared by slowly adding a solution of stannous chloride in dilute hydrochloric acid to a heated solution of sodium carbonate, filtering the precipitate, washing with distilled water, and drying.



TABLE IV. RESULTS OF TESTS WITH STANNOUS OXIDE  
Yield of Volatile Products, Per Cent of Ash- and  
Moisture-Free Coal

Stannous Oxide, Per Cent of Charge	Without Vehicle		With Vehicle	
	Total	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0096	63.8	9.0	72.7	14.2
	63.6	8.9	74.1	15.1
0.0951	68.9	14.6	79.4	20.2
	69.7	15.4	79.5	20.1
0.899	75.7	21.5	82.1	22.5
	75.7	21.4	82.4	22.6
4.56	80.6	26.2	83.3	23.3
	80.5	26.0	83.7	23.5
9.51	80.5	25.7	84.4	24.1
	80.4	25.2	83.6	23.1

When the stannous oxide was treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-47	12.23
2-48	12.25

The proportion of tin in stannous oxide ( $\text{SnO}$ ) is 88.12 per cent, and in stannous hydroxide [ $\text{Sn}(\text{OH})_2$ ] is 77.73 per cent. The residual tin was 87.76 per cent of the charge. It was in the form of small spheres.

The results of the test with varying proportions of stannous oxide, in the presence and absence of the vehicle, are given in Table IV.

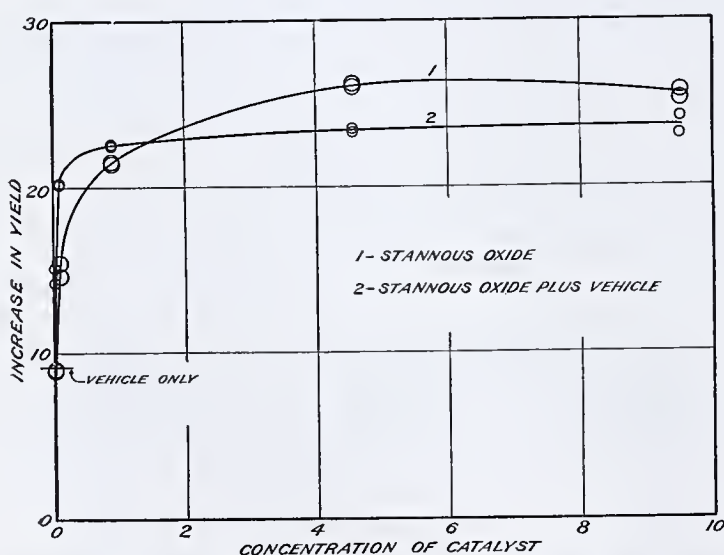


FIGURE 3. INCREASE IN YIELD DUE TO STANNOUS OXIDE  
(DATA FROM TABLE IV)

Part of the data of Table IV is shown graphically in Figure 3. Curve 1 gives the increase in yield due to the catalyst in the absence of the vehicle. Curve 2 gives the increase due to the combined catalyst and vehicle; it therefore cuts the line of zero catalyst at 9.1 per cent, which is the average increase in yield due to the use of the vehicle.

**STANNOUS OXALATE.** Stannous oxalate is one of a number of organic compounds of tin claimed as catalysts for coal hydrogenation in British Patent 363,445 (1). It has been stated that this type of compound is used in the commercial hydrogenation plant of Imperial Chemical Industries at Billingham, England (3). The sample used for these tests had been prepared by precipitation from stannous chloride solution by potassium oxalate solution.

When it was treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-51	43.13
2-52	43.19
Av.	43.16

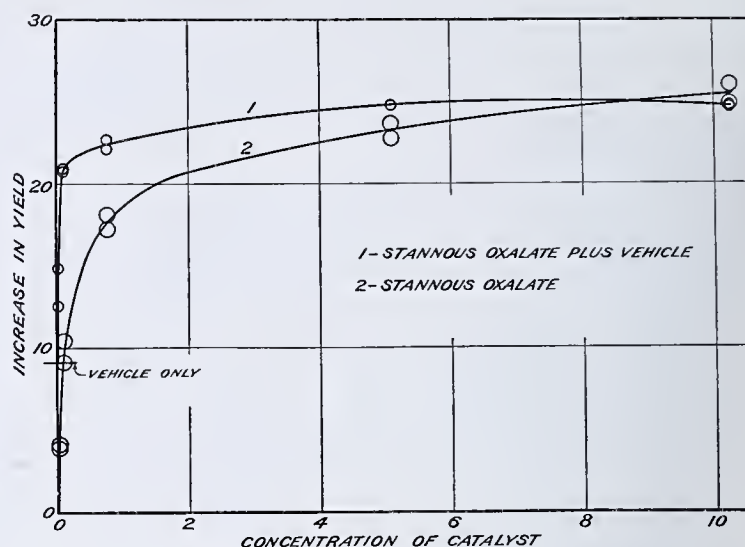


FIGURE 4. INCREASE IN YIELD DUE TO STANNOUS OXALATE  
(DATA FROM TABLE V)

TABLE V. RESULTS OF TESTS WITH STANNOUS OXALATE  
Yield of Volatile Products, Per Cent of Ash- and  
Moisture-Free Coal

Stannous Oxa- late, Per Cent of Charge	Without Vehicle		With Vehicle	
	Total	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0104	60.0	3.9	72.0	14.8
	60.2	4.1	69.8	12.5
0.0955	66.4	10.4	78.0	20.7
	65.0	9.1	78.5	20.9
0.773	73.0	17.2	80.4	22.7
	73.5	18.1	79.9	22.1
5.09	78.1	22.8	82.7	24.8
	78.9	23.7	82.9	24.8
10.24	79.9	24.9	82.7	24.5
	80.9	26.0	83.0	24.7

The residue is, therefore,  $100 - 43.16 = 56.84$  per cent of the charge. The proportion of tin in stannous oxalate is 57.43 per cent. The residual tin was in the form of spheres, much the same as those produced from the stannous oxide, but having a larger average size.

The results of the tests with varying proportions of stannous oxalate are given in Table V, and shown graphically in Figure 4.

**AMMONIUM MOLYBDATE.** Compounds of molybdenum are good catalysts for the hydrogenation of coal tars, but have been considered inferior to tin compounds for the liquefaction of coal. Ammonium molybdate was included in these tests, because it had previously been studied in comparison with other catalytic materials (4), and because it was a compound of a multivalent element which could be partly reduced under the conditions of the test.

When treated alone under the conditions of the test, the loss in weight was as follows:

Test No.	Loss in Weight, Per Cent of Charge
2-45	25.29
2-46	25.12
Av.	25.21

The residue was, therefore,  $74.79$  per cent of the original ammonium molybdate. If only molybdenum trioxide had been formed, the residue would have been  $81.53$  per cent of the charge, and if only the dioxide it would have been  $72.47$  per cent. The residue was also used as a catalyst.

The results of the tests with ammonium molybdate and with the residue are given in Tables VI and VII, and shown graphically in Figure 5. In Figure 5, curve 3, the dotted line is made by plotting the concentration of ammonium molyb-



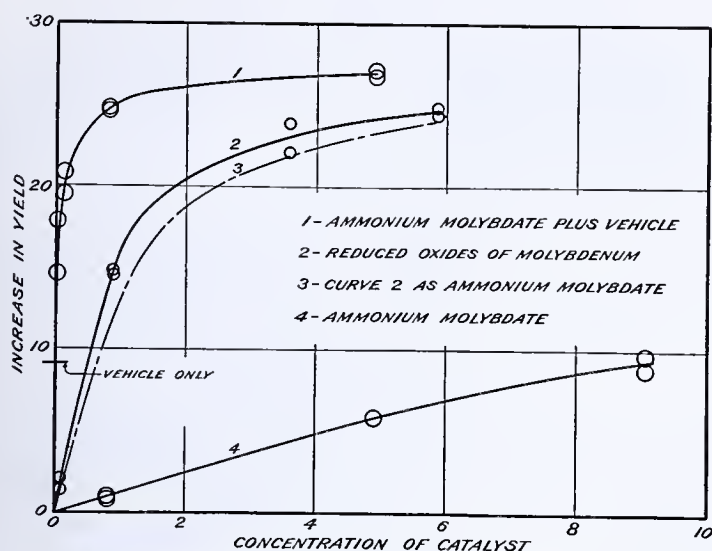


FIGURE 5. INCREASE IN YIELD DUE TO AMMONIUM MOLYBDATE AND REDUCED AMMONIUM MOLYBDATE (DATA FROM TABLES VI AND VII)

TABLE VI. RESULTS OF TESTS WITH AMMONIUM MOLYBDATE

Ammonium Molybdate, Per Cent of Charge	Yield of Volatile Products, Per Cent of Ash- and Moisture-Free Coal		With Vehicle	
	Without Vehicle	Increase due to catalyst	Total	Increase due to catalyst + vehicle
0.0145	57.6	0.6	75.1	14.6
	55.7	-1.5	78.1	17.8
0.121	58.2	0.9	80.9	20.8
	56.2	-1.2	79.3	19.5
0.817	58.4	1.0	84.2	24.8
	58.2	0.8	83.6	24.6
4.91	63.2	5.8	85.7	27.2
	63.1	5.8	83.0	26.8
9.06	66.0	8.8	84.7	..
	66.8	9.7	83.6	..

TABLE VII. RESULTS OF TESTS WITH REDUCED AMMONIUM MOLYBDATE

Reduced Molybdate, Per Cent of Charge	Yield of Volatile Products, Per Cent of Ash- and Moisture-Free Coal,	
	Total	Increase due to catalyst
0.0070	57.5	-0.4
	58.0	0.3
0.0825	59.0	1.4
	59.6	2.1
0.889	71.9	14.5
	72.0	14.8
3.59	81.1	23.9
	79.3	22.1
5.86	81.6	24.4
	82.1	24.9

date required to produce the corresponding concentration of residue shown in curve 2.

### Discussion

The effect of catalysts in small concentrations is pronounced. For instance, 0.01 per cent of stannous oxide brings about the production of nine hundred times its own weight of volatile material. However, in high concentrations the catalysts are much less efficient, and there is practically no increase in yield when the catalyst concentration is increased beyond 5 per cent. Suitable concentrations for test purposes, therefore, would be 1 per cent in the absence and 0.1 per cent in the presence of a vehicle.

The vehicle renders the catalysts more effective in small concentrations, but slightly decreases their efficiency at high concentrations. It tends to eliminate differences in their efficiency, and for this reason comparative tests of catalytic

materials would probably be more informative in the absence of a vehicle.

The effect of preliminary reduction in the absence of coal increases the efficiency of ammonium molybdate. It is advisable, therefore, to make comparative tests on both reduced and nonreduced materials. The preliminary reduction, when carried out quantitatively, also serves to indicate the state of combination in which the catalyst exists under the conditions of the test.

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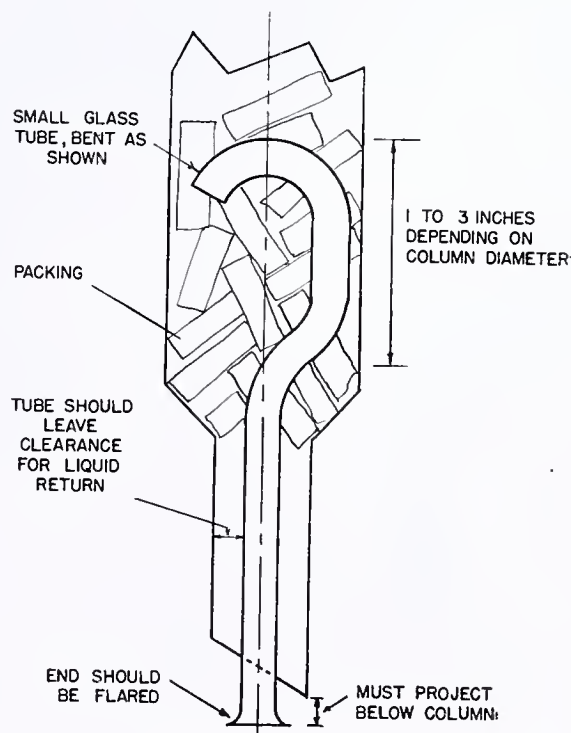
## Laboratory Fractionating Column

GEORGE F. REYLING

Foster D. Snell, Inc., Brooklyn, N. Y.

SMALL packed laboratory fractionating columns with constricted bases often tend to become filled with condensed liquid which cannot return to the flask because of pressure of the rising vapors. Consequently the column becomes filled with liquid and fails to operate properly when near its maximum capacity.

This condition may be alleviated by placing a glass tube, bent as shown in the diagram, in the bottom of the column. This arrangement permits return of the condensed liquid to the flask, and at the same time allows the vapors to pass unhindered to the top of the column.





# Analysis of Fusel Oil by Azeotropic Distillation

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DURING the process of fermentation as normally applied in the production of ethyl alcohol, the starting raw materials contain proteins and amino acids which by the action of enzymes and yeast (8) produce a product known as fusel oil. The major portion consists of alcohols boiling between ethyl and hexyl and small amounts of ethyl alcohol, water, acids, esters, furfuraldehydes, and higher boiling alcohols. In Table I are shown results of the analysis of fusel oil by previous investigators.

TABLE I. ANALYSIS OF FUSEL OIL

	Type of Mash			
	Mandya molasses (6)	Kaoling (5)	Molasses (5)	Sweet potatoes (5)
Water	18	..	..	..
Acid	0.1	..	..	..
Ethyl alcohol	8	..	..	..
Isopropyl alcohol	0.5	..	..	..
<i>n</i> -Propyl alcohol	18	6.3	1.8	..
Isobutyl alcohol	5.5	0.6	..	..
<i>n</i> -Butyl alcohol	6	..	..	..
Active amyl alcohol	41	17.5	12.4	77.4
Isoamyl alcohol	3	66.7	50.7	12.9
<i>n</i> -Amyl alcohol	3	..	..	0.5

These indicate that the qualitative and quantitative aspects of fusel oil depend on many factors and are not controlled alone by the type of mash used. The other factors may be (a) type of yeast or enzyme used for fermentation, (b) condition and environment under which fermentation proceeds, and (c) method of recovery of fusel oil from the rectifying column (3). These facts were corroborated by the results of the present investigation in which the fusel oil fractions used were produced from almost identical "mash bills" in two different distilleries.

In Table II are given the weight percentage amounts of the alcohols found in the two samples of fusel oil, produced from mash containing more than 90 per cent corn. The results, as given, are calculated on the total weight of alcohols present, and are not representative of the fusel oil fractions as received. The amounts of water and ethyl alcohol present depend on the method used for concentrating the fusel oil fraction and, therefore, should not be included in the calculations.

The residues obtained during the initial distillation procedure were too small in volume to continue the distillation. However, upon combining them, about 60 per cent was re-

covered as isoamyl alcohol by further distillation. This indicates that if *n*-amyl alcohol was present its amount would be considerably below 1 per cent of the alcohol fraction.

## Experimental Procedure

To rid them of the excess water and ethyl alcohol, the samples were treated with saturated salt solution, and the fusel oil was recovered by extraction with carbon tetrachloride. The extract thus obtained was subjected to atmospheric distillation in a modified 120-plate bubble cap column (2). The presence of the carbon tetrachloride facilitated the removal of the small amounts of water and ethyl alcohol still present in the mixture, by virtue of the low-boiling ternary azeotrope formed by water, ethyl alcohol, and carbon tetrachloride (4). By continued azeotropic distillation all the *n*-propyl alcohol and isobutyl alcohol were removed, leaving in the pot the alcohols boiling above *n*-butyl alcohol. However, because of an insufficient amount of carbon tetrachloride some isobutyl alcohol remained behind and was distilled along with the active amyl and isoamyl alcohols.

TABLE II. ALCOHOLS IN FUSEL OIL

Alcohol	Distillery A	Distillery B
	Wt. %	Wt. %
<i>n</i> -Propyl	20.4	1.7
Isobutyl	23.9	12.2
Active amyl	14.6	23.4
Isoamyl	36.3	59.7
Residue	4.8	2.96

In Figure 1 is shown the separation occurring during the distillation according to boiling point (curve 2), refractive index (curve 1), and specific rotation (curve 3). On curve 2, A indicates the ternary azeotrope water-ethyl alcohol-carbon tetrachloride, B the binary azeotrope *n*-propyl alcohol-carbon tetrachloride, and C the binary azeotrope isobutyl alcohol-carbon tetrachloride.

There was no indication of the presence of isopropyl alcohol. However, to be sure, plateau A was subjected to further extraction and subsequent distillation procedure, the results of which indicated the absence of isopropyl alcohol.

Curves 1 and 2 respond alike to change. The low dip of curve 1 located near 2900 ml. is due to the presence of some

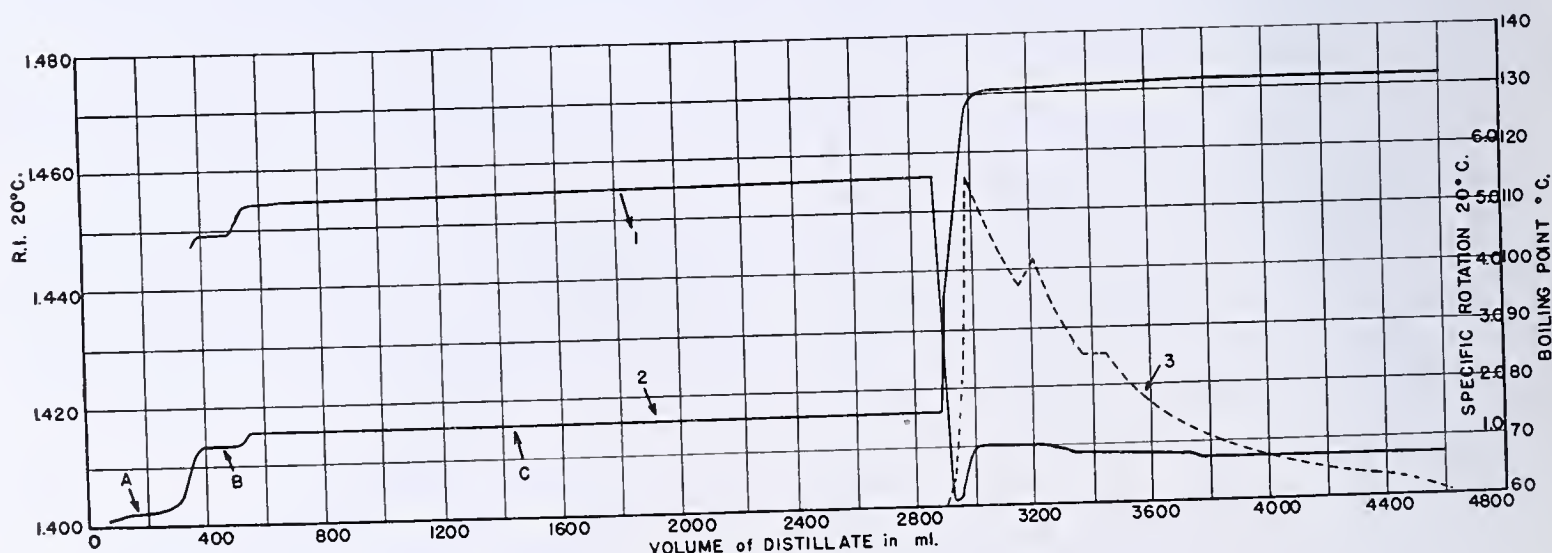


FIGURE 1. SEPARATION DURING DISTILLATION



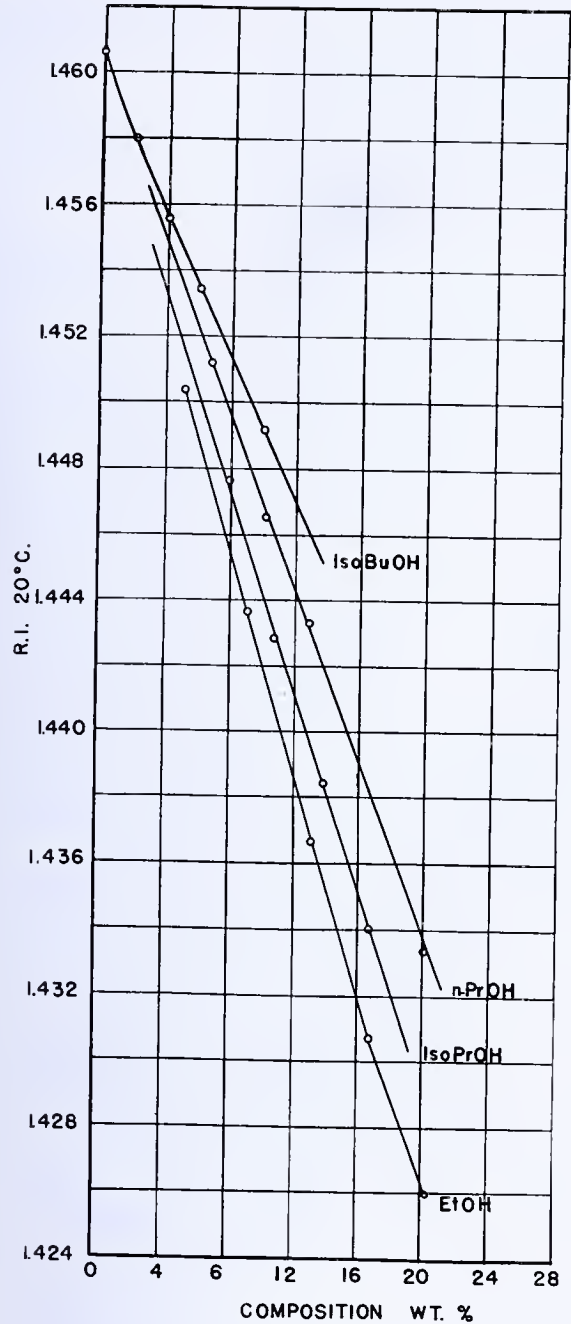


FIGURE 2

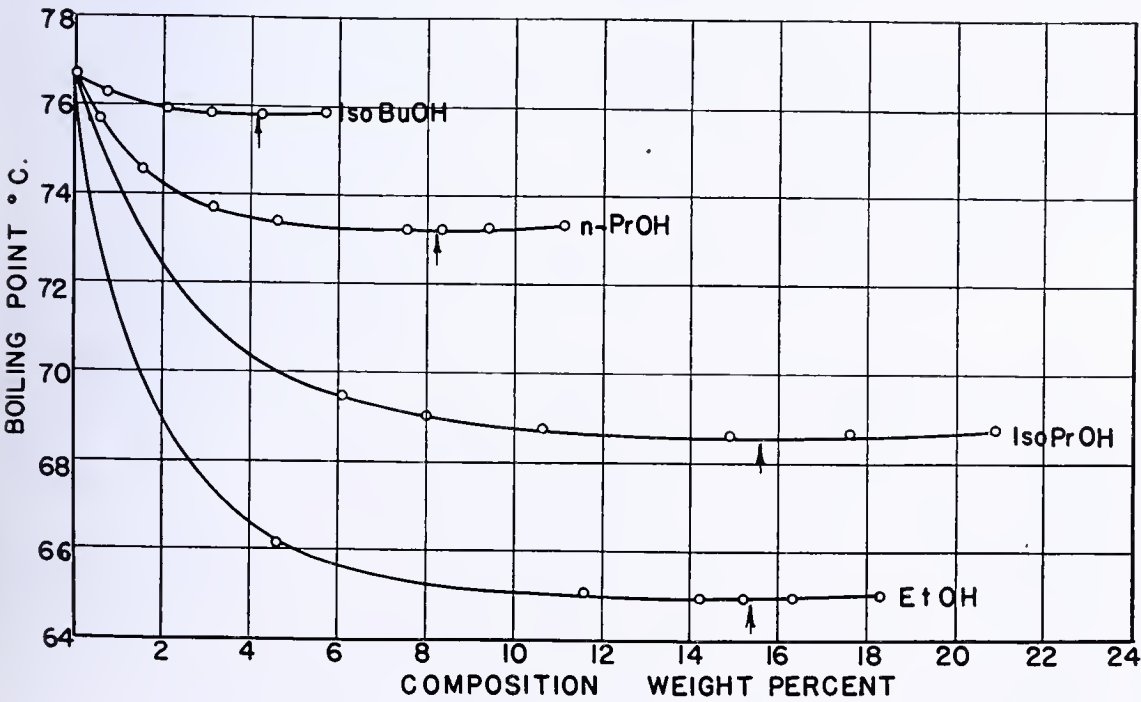


FIGURE 3. AZEOTROPIC CURVES OF ALCOHOLS WITH CARBON TETRACHLORIDE

isobutyl alcohol, which remained in the residue in the pot because of insufficient quantities of carbon tetrachloride to form the azeotrope.

The irregularities noted in curve 3 are due to the intermittent distillation procedure used. The still was not run continuously, and consequently on starting each day there were produced abnormal conditions which were most evident in the specific rotation determinations. It is interesting to note that one fraction was obtained which had the value  $[\alpha]_D^{20} - 5.57$ . Accordingly, using the value for pure *l*-amyl alcohol of  $[\alpha]_D^{20} - 5.78$  the purity was calculated as 96.3 per cent (1).

The alcohols—*n*-propyl, isobutyl, and isoamyl—were identified as the phenyl urethane derivatives. The urethanes were prepared directly from the azeotropic mixtures by refluxing approximately 10 ml. of azeotrope with 1 ml. of phenyl isocyanate for 20 minutes. A small amount of sodium bicarbonate was added to aid the reaction. After refluxing, the carbon tetrachloride was removed by evaporating on the steam bath and the urethane taken up in hot petroleum ether from which it precipitated upon cooling.

The melting point of some of the derivatives thus formed did not agree with the values given in the literature. However, the same melting points were obtained independent of either the method of preparation or the source of the alcohol.

TABLE III. MELTING POINTS

Alcohol	Found ° C.	Phenyl Urethane Literature ° C.
Ethyl	51–51.5	52
Isopropyl	87	90
<i>n</i> -Propyl	51.5	58
Isobutyl	85.5–86	80
<i>n</i> -Butyl	59.5	57
Isoamyl	55	55

In Table III are given the melting points as found by experiment and those given in the literature (7). Although the melting points of the urethanes obtained from ethyl and *n*-propyl alcohols are the same, mixed melting points are definite proof that the derivatives are not the same. It is to be noted also that the melting points of the urethanes of isobutyl and *n*-butyl alcohols are higher than the values given in the literature.

The amount of alcohol in the azeotropic mixtures was determined by refractive index measurements. However, since the solutions formed by carbon tetrachloride with the alcohols are abnormal, it was necessary to determine experimentally the relation between refractive index and composition. The curves are given in Figure 2 and show the change of refractive index  $n_D^{20}$  with change in composition for ethyl, isopropyl, *n*-propyl, and isobutyl alcohols.

From the weight of the distillate and its refractive index the weight of alcohol present was obtained.



### Azeotropes

It was noted during the investigation that in certain mixtures, the molal composition and boiling point of the azeotrope did not check with the values as given in International Critical Tables. Consequently the composition and boiling points of the azeotropes of ethyl, isopropyl, *n*-propyl, and isobutyl alcohol with carbon tetrachloride were determined.

TABLE IV. AZEOTROPE VALUES

Alcohol	Experimental Values			International Critical Tables		
	B. P. ° C.	Alcohol Mole %	Pressure Mm. Hg	B. P. ° C.	Alcohol Mole %	Pressure Mm. Hg
Ethyl	64.92	38.0	760.4	64.95	39	760
Isopropyl	68.6	32.1	762.5	67.0	36.0	760
<i>n</i> -Propyl	73.2	18.7	763.5	72.8	25	760
Isobutyl	75.75	8.2	762.5	75.8	11	760

In Table IV is given a comparison of the values obtained with those given in International Critical Tables (4). The discrepancies between the observed and reference values may be assumed as real, and not totally dependent on the slight variation in pressures existing during the determinations.

TABLE V. ALCOHOL VOLUME

Alcohol	Alcohol to Produce 100 Ml. of Azeotrope Ml.
Ethyl	26.9
Isopropyl	27.3
<i>n</i> -Propyl	15.1
Isobutyl	7.86

In Figure 3 are shown the azeotropic curves of the alcohols with carbon tetrachloride. Because of the flatness of the curves, it was impossible to obtain the correct value for the composition of the azeotrope by visual inspection. Accordingly, the true values were obtained by subjecting the mixtures of the various alcohols and carbon tetrachloride to a distillation in a 90-cm. (3-foot) column packed with small glass helices. The molal composition of the azeotrope was then determined by measuring the refractive index of the distillate, and referring to the curves in Figure 2.

### Apparatus

In Figure 4 is shown the Cottrell boiling point apparatus used in the determination of the azeotropes.

The lower tube on the apparatus, A, is the boiler, and is coated on the inner surface with a layer of Carborundum fused into the glass. This ensures uniform and even boiling at all times. Heat is applied by means of a heating coil made of B. & S. gage No. 22 Nichrome wire wrapped directly on the tube itself. To obtain uniform heating conditions, the boiler is lagged with a 1.25-cm. (0.5-inch) layer of magnesia cement.

The boiling points were determined by means of a 4-junction copper-constantan thermoelement and a Leeds & Northrup potentiometer No. 248,801.

### Discussion

By azeotropic distillation, the qualitative and quantitative estimation of alcohols boiling below *n*-butyl and present in fusel oil is simplified. The advantage of this procedure is threefold: The water present is removed at the beginning and does not interfere with the distillation; efficient distillation units are not necessary for complete separation; and because of the low percentage of alcohols present in the azeotropes, it is possible to proceed with small samples of fusel oil. In other words, the distillable volume is increased to the point where the factor of holdup of the distillation unit need not enter into the problem. In Table V are given the volumes of alcohols necessary to produce 100 ml. of azeotrope.

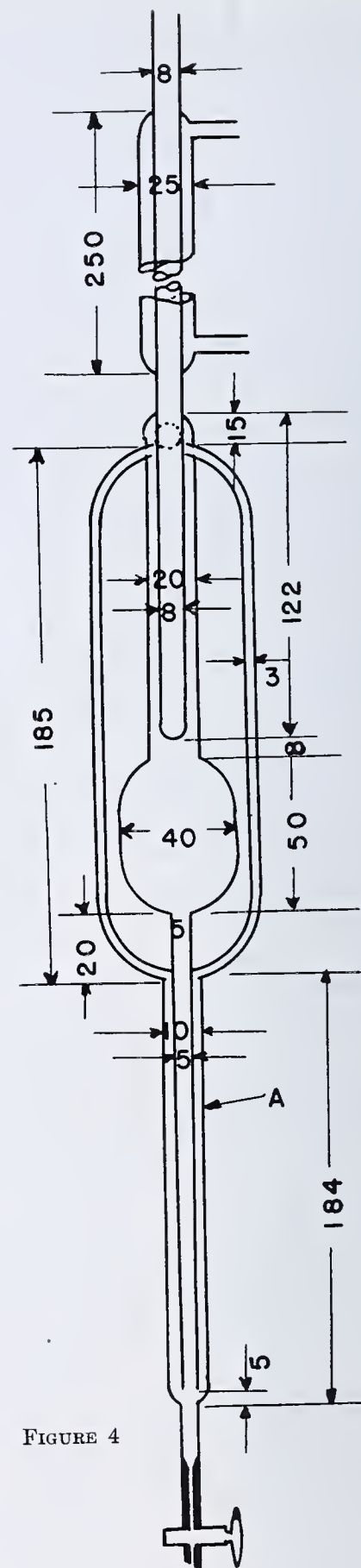


FIGURE 4

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# Quantitative Estimation of Phenol and Related Compounds in Tissues

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THE amount of phenol present in normal tissues has been the subject of many investigations, but the results are on the whole very conflicting. This disagreement is apparently due, not only to variation in the tissues, but also to the variety of methods employed in determining the phenol and the failure, in the older methods, to separate this compound from substances that react in a similar manner. [Reviews of these older methods have been given by Tisdall (16), Pelkan (11), and Smith (14)].

More recently, however, these errors have been recognized and procedures have been proposed which determine only the truly phenolic substances. In general these methods are based on differences in the volatility and solubility of the substances present with the phenols.

Haas and Schlesinger (7) determined the volatile and non-volatile phenols of whole blood, using Millon's reagent. Smith (14) estimated the volatile phenols of various tissues by treating the distillate from a trichloroacetic acid extract with the Folin and Denis reagent (5). His results are much lower than those obtained by other investigators who did not employ the distillation step (1, 4, 11, 12, 15). Marcolongo (8, 9) distilled oxalated or citrated whole blood from a sodium bicarbonate solution and extracted the volatile phenols in the distillate with ether. He recommended Moir's reagent (10), diazotized *p*-nitroaniline, as being specific and sensitive for phenols, and avoided the use of sulfuric and phosphoric acids as protein-precipitating agents because he noted high results when they were used. In his second paper Marcolongo carried the phenol separation further by extracting the distillation residue of a Folin-Wu blood filtrate with ether, which was then extracted with 4 to 5 per cent of sodium hydroxide to remove the "oxy-acids" from the diphenols which he stated remained in the ether.

Barac (2), in a study of the hydrolysis of potassium phenol sulfate, removed the blood proteins with Folin-Wu reagent, extracted the phenols with ether, and determined them spectrographically. His results showed 100 per cent recoveries of phenol added to blood. Schmidt *et al.* (13), after extensive studies on the phenol and imidazole content of blood, conclude that "practically the entire 'diazo value' of the blood, generally reported in the literature as phenol, is actually made up of ether-insoluble compounds." They used a continuous ether extraction and obtained recoveries of added phenol of from 51 to 82 per cent. With this method they found approximately 0.02 mg. of phenol in 100 ml. of pooled human blood.

In the course of a study in this laboratory on the toxicology of certain chlorinated phenols it became necessary to have a method by which the true total phenol content of tissues could be determined as accurately as possible. The accompanying scheme of separation was adopted.

Preliminary results seem to offer some explanation for discrepancies reported in the past.

Initial studies with trichloroacetic acid filtrates gave high results when phenol was added to the tissue. The source of error appeared to be a neutral volatile substance which was formed during the distillation. This substance could be removed by distilling the phenols into an alkaline solution, which was then evaporated to a small volume. When this procedure was followed, control experiments without tissue gave almost perfect recoveries, but the recovery of phenol added to blood was poor, indicating a loss before or during the distillation. Results obtained by this method in the past are therefore open to question.

Precipitation of the tissue proteins with the Folin-Wu reagent from an aqueous extract of the ground tissue proved to be more satisfactory. Steam-distillation of the filtrate into alkali and evaporation of the distillate gave recoveries of phenol ranging from 68 to 90 per cent of the amount added to blood. Apparently some phenol was carried down with the protein precipitate (3, 7).

In order to determine the effect of interfering compounds on the colorimetric determination of phenol with the Moir reagent, a number of compounds that might theoretically be present in tissue were treated with this reagent and their approximate phenol equivalents were estimated.

## Reagents Required

A standard solution of phenol containing 0.1 mg. of phenol in 1 ml. of 0.1 *N* hydrochloric acid (6). The working standard containing 0.003 mg. of phenol in 1 ml. of 0.1 *N* hydrochloric acid was prepared weekly from this solution.

Sulfuric acid, 0.67 *N*

Sodium tungstate, 10 per cent

Sodium hydroxide, 0.5 and 4 per cent

Sodium acetate solution, 25 per cent, in aqueous gum acacia, 0.5 per cent

A solution containing 1.5 grams of *p*-nitroaniline dissolved in 40 ml. of hydrochloric acid (sp. gr. 1.19) was diluted to 500 ml.

The Moir reagent was prepared daily by treating 25 ml. of this solution with 0.75 ml. of sodium nitrite, 10 per cent (10). Sodium carbonate, 20 per cent Hydrochloric acid, 10 per cent Sand, Ottawa Ether, U. S. P.

## Procedure

The organ was ground, mixed with 10 ml. of water, and pulped with dry sand in a mortar. It was then washed into a flask with 30 ml. of water and treated with 20 ml. of sodium tungstate solution, followed by 20 ml. of sulfuric acid added dropwise from a buret. In the case of blood, 20 ml. of oxalated blood were

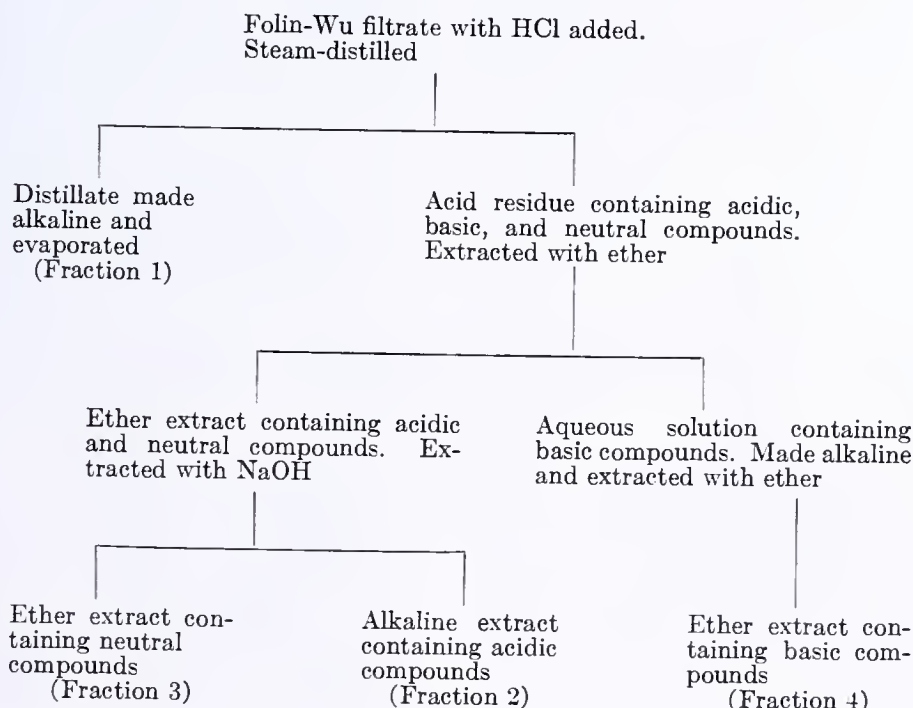




TABLE I. RECOVERY OF PHENOL ADDED TO RABBIT BLOOD AND MUSCLE

(Determined by steam-distillation)

Tissue	Phenol Originally Present Mg. %	Phenol Added Mg. %	Total Phenol Found Mg. %	Added Phenol Recovered %
Blood	0.318	0.996	1.046	73.0
	0.247	2.000	2.042	89.7
	0.255	2.000	1.760	75.3
	0.150	2.000	1.880	86.5
	0.171	2.000	1.524	67.7
	0.185	3.000	2.850	88.8
	0.195	3.000	2.400	73.5
	0.250	3.000	2.500	75.0
Muscle	0.250	2.000	1.880	81.5
	0.200	2.000	1.853	82.7

TABLE II. DISTRIBUTION IN NORMAL RABBIT TISSUES OF SUBSTANCES WHICH REACT AS PHENOL

(Expressed in milligrams per 100 grams of tissue)

Tissue	Fraction 1 (Volatile Acidic)	Fraction 2 (Nonvolatile Acidic)	Fraction 3 (Nonvolatile Neutral)	Fraction 4 (Basic)
Blood	0.16-0.24	0.15-0.33	0.03-0.07	0.06-0.08
Brain	0.19-0.25	0.34-0.55	0.05-0.06	0.02-0.07
Heart	0.14-0.24	0.21-0.54	0.00-0.07	0.04-0.09
Kidney	0.19-0.51	0.42-0.78	0.12-0.16	0.14-0.18
Lungs	0.18-0.24	0.32-0.53	0.05-0.10	0.08-0.13
Stomach	0.11-0.24	0.23-0.43	0.03-0.04	0.08-0.10
Fat	0.09-0.23	0.12-0.27	0.04-0.07	0.04-0.07
Liver	0.12-0.22	0.15-0.54	0.04-0.09	0.05-0.09
Muscle	0.13-0.22	0.12-0.33	0.05-0.07	0.06-0.07

diluted with 40 ml. of water and after 10 minutes the proteins were precipitated as above. After standing for at least 15 minutes the mixtures were filtered. When the customary 20-gram sample was used, 1 ml. of the filtrate represented 0.2 gram of tissue. Samples of 20 grams or more should be used, although 10-gram samples gave reproducible results.

A known volume of the filtrate was placed in a 250-ml. flask equipped with a ground-glass joint and 1 ml. of concentrated hydrochloric acid was added for each 25 ml. of the filtrate. The flask was connected to an all-glass distillation apparatus and the contents were distilled with steam, the volume being kept constant. Approximately 270 ml. of distillate were collected in a flask containing 2 ml. of 4 per cent sodium hydroxide, evaporated slowly on a hot plate to 8 to 10 ml., and then filtered into a 50-ml. graduated cylinder. The flask and filter were washed until the filtrate reached a volume of 20 ml. A standard containing 0.015 mg. of phenol in 20 ml. was prepared from the stock solution. Four milliliters of sodium acetate-gum acacia were added to each solution, followed by 2 ml. of the diazotized *p*-nitroaniline and, after 1 minute, by 4 ml. of sodium carbonate. The solutions were compared in a colorimeter after 3 minutes. The volatile phenols (fraction 1) were calculated from this result.

The distillation residue was concentrated to 100 ml., filtered into a separatory funnel, and then extracted with five 25-ml. portions of ether. The aqueous solution was saved for the determination of basic compounds (fraction 4). The ether solution was extracted with 5 ml. of 4 per cent sodium hydroxide and 20 ml. of water. If the extract was not alkaline the extraction was repeated with the same solution after a further addition of alkali (2 ml.), and the ether was then extracted with four 25-ml. portions of 0.5 per cent sodium hydroxide. In order to obtain a sharp separation of the neutral compounds it was necessary to extract the combined alkaline solutions twice with 25-ml. portions of ether, which were then added to the original ether solution. The latter contained the nonvolatile ether-soluble neutral compounds (fraction 3).

The alkaline solution was neutralized to litmus with 10 per cent hydrochloric acid and evaporated to 5 to 8 ml. It was then filtered and made up to 20 ml., and the phenols were determined by the procedure used for fraction 1. The nonvolatile ether-soluble acidic compounds (fraction 2) were calculated as phenol from this result.

The ether extract containing fraction 3 was mixed with 5 ml. of water containing a drop of 10 per cent hydrochloric acid. The ether was then evaporated on a water bath kept below 80°. The residue was filtered into a 50-ml. cylinder and made up to 20 ml. In most cases the color developed was very weak and the final estimation was carried out by comparing this unknown with a series of standards containing 0.000, 0.003, 0.006, 0.009, 0.012, and 0.015 mg. of phenol made up to the same volume. The comparison was made in test tubes. The result indicated the quantity of the compounds in fraction 3 expressed in terms of phenol.

The aqueous solution containing fraction 4 (from the first extraction) was made just alkaline to litmus with 4 per cent sodium hydroxide and extracted 5 times with 25-ml. portions of ether. The combined ether solution was treated in the same manner as that which contained fraction 3 and the color developed was determined in the same way. The total ether-soluble basic compounds were calculated as phenol from this result.

With careful work the results were reproducible. It is essential that sharp separations be obtained in the extraction steps, that the water used be free from phenols, and that the colorimetric readings be taken promptly 3 minutes after the addition of the alkali.

## Results

Table I gives the results obtained when phenol was added to normal tissues and recovered by steam distillation as described.

Table II gives the results when the tissues of four normal rabbits were used to determine the normal tissue content of substances which react as phenol.

The substances which may theoretically be present in normal tissue extracts are given in Table III, classified according to the fraction in which they should occur.

TABLE III. CLASSIFICATION OF COMPOUNDS WHICH MAY BE PRESENT IN EXTRACTS OF NORMAL TISSUE

(Figures show approximate molar concentrations which give a color equivalent to 0.00001 molar phenol solution when Moir's reagent is used.)

Fraction 1 <sup>a</sup>	Fraction 3
Phenol	Lecithin
<i>p</i> -Cresol (0.0025?)	$\beta$ -Nicotinamide
Pyruvic acid (0.0005)	Indican
Formic acid (no color)	Urea (0.22)
Butyric acid (no color)	
Higher fatty acids	Fraction 4
	Choline (0.13)
Fraction 2	Taurine
$\beta$ -Hydroxybutyric acid	Indole (0.02?)
Acetoacetic acid	Histamine
Homogenistic acid	Aliphatic amines of low molecular weight
$\beta$ -Nicotinic acid	
Hydroquinone (0.00005)	
Catechol (0.000025)	
Hippuric acid (0.04)	
Ethyl mercaptan (no color)	

<sup>a</sup> The alkaline evaporation of the distillate removes acetone (0.07), ethyl alcohol (0.09), acetaldehyde (0.00028), and methyl glyoxal.

## Summary

A method is reported for the separation and determination of volatile phenols, free and conjugated, in tissues. The non-volatile ether-soluble substances present have been separated into three fractions—acidic, neutral, and basic—and the extent to which they react as phenol has been determined.

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# Apparatus for Determining Moisture by the Distillation Method

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THE continued interest in the distillation method for the determination of moisture (1, 2, 3) in materials containing no low-boiling liquids appreciably miscible with water lies in the fact that it measures only the actual water which is given off at the boiling temperature of the liquid used, whereas by the oven methods the total loss in weight is obtained. Total loss includes, besides the true moisture content, the weight of other volatile constituents of the material under examination, plus the weight of any water that may be formed from the oxidation of the nonvolatile constituents, minus any gain in weight due to the formation of nonvolatile oxidation products.

In the usual Bidwell-Sterling apparatus, as well as in any modification of which the authors are aware, it is necessary to bring the moisture clinging to the walls of the condenser into the measuring tube either by the use of a buret brush or by the introduction of some substance (1, 2, 3) to reduce its tendency to adhere to the glass. Using the apparatus described in this paper, it is unnecessary to resort to such practices. The entire determination may be completed in less than 2 hours.

The general procedure, which can readily be gathered from

the diagram, is as follows: The water and toluene, which are distilled from a flask immersed in an oil bath, pass through a slanted tube and down through a condenser whose outlet is beneath the toluene in the measuring vessel.

The advantages of locating the condenser on the downcoming tube are not immediately apparent but become so when compared with the operation of the condenser in other locations. In the Bidwell-Sterling apparatus the vapors of toluene and water travel up into the reflux condenser, condense, and flow back by gravity. Most of the water condenses above the toluene, and the droplets which cling to the glass can be dislodged only by additional manipulation.

In the early forms of the apparatus described in this paper and in an apparatus recently reported by Avellar de Loureiro (1) the condenser was placed around the receiver. Under these conditions the distillate tended to form a milky suspension of water in toluene from which the droplets of water were deposited on the cooled walls of the receiver to probably the same degree as with the original Bidwell-Sterling apparatus. It was not possible for the condensed toluene to flow over these droplets, and some method of bringing the droplets into the measuring tube was necessary. On the other

hand, with the condenser on the downcoming tube, all the droplets of water deposited on the cold walls of the condenser are washed by the condensing toluene or are dislodged by the surging toluene mentioned below in connection with the bumping. The milky suspension, which practically always forms except with samples having a very low moisture content, is not circulated past cold walls.

Strangely enough, no considerable amount of milky suspension or toluene distillate ever accumulates in the upper part of the receiver. This results from the automatic sucking-back caused by the building up of the column of distilled toluene in the cooled tube leading down from the flask, along with the vigorous surging caused by the bumping in the distillation flask. When the column of toluene builds up to a sufficient height, the surging causes some of the cooled condensate to drop into the distilling flask; and the resultant cooling effect causes the entire liquid, down to the outlet of the condenser, to be sucked back into the distillation flask. The frequency of this operation depends on the rate of distillation; usually it occurs about once every 10 minutes.

The bumping is, of course, an almost invariable accompaniment to the determination of moisture in solid foodstuffs by the distillation method. Its violence may be reduced by immersing the distilling flask in a bath to bring about more uniform heating. However, when bumping was entirely eliminated—for example, by placing the sample in a cloth bag and suspending it in the toluene—neither the surging nor the automatic suck-back took place. When distilled water was added to the toluene in order to determine the extent of its recovery, the surging and suck-back were likewise not observed. On adding a small quantity of dry sand to the toluene-water mixture the bumping once more occurred, and the distillation proceeded entirely unaided.

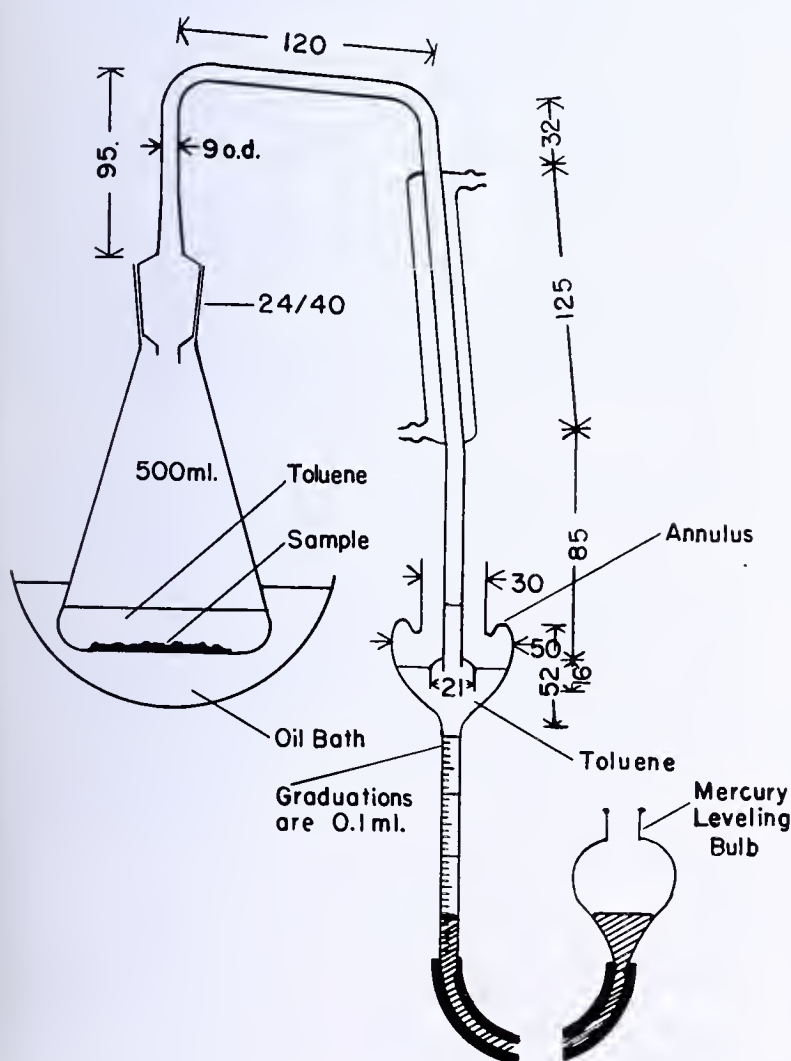


DIAGRAM OF APPARATUS  
Dimensions in millimeters



The repeated automatic suck-back is important to the determination of the moisture by this method. Careful observation of the progress of the distillation of the water shows that the first portions which come over condense in large clear drops and quickly sink into the measuring vessel; later, the condensed droplets become very small and the milky suspension results. As a consequence of the repeated suck-back, the fine droplets are repeatedly distilled, and each time this occurs a considerable number of clear droplets sink into the measuring tube, with the final result that the determination is completed with no supernatant suspension. This condition is frequently reached in 1 hour, although in some cases it may require 2 hours or more.

Since it is impossible to control the bumping accurately, two other points should be emphasized—namely, the use of an enlarged or bell-shaped end on the condenser tube and an annular ring on the receiver. The function of the enlarged end is to reduce the violence with which the liquid is driven into the receiver. However, in spite of this provision an especially violent bump will occasionally drive the toluene up the sides of the receiving vessel with sufficient velocity to cause a drop or two of liquid to splash out. The insertion of the annular ring eliminated this loss by causing the liquid to be thrown back into the center of the receiver.

The mercury leveling bulb connected to the bottom of the graduated receiver proved advantageous at times in collecting droplets clinging to the sides of the measuring tube and in

leveling the top meniscus of the water layer in order to facilitate reading.

A series of moisture determinations was made on ground soybeans with the following results: 6.73, 6.64, 6.71, 6.59, 6.73, and 6.80 per cent. The maximum difference in this series is 0.21 per cent, whereas the maximum difference due to the error in reading the graduated measuring tube, assuming it can be read to  $\pm 0.01$  cc. would be 0.134 per cent, since the total volume of water obtained is about 1.00 cc. The samples used weighed 15 grams to the nearest milligram. The temperature of the oil bath surrounding the distillation flask varied from 110° to 155° C.

### Summary

An apparatus for the determination of moisture has been devised and has been found to be superior to those of the Bidwell-Sterling type, because the removal of droplets of water forming on the walls of the condenser is accomplished automatically and the milky suspension forming in the receiver is eliminated by automatic redistillation.

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## Determination of Neutral Oil and Tar Acids in Phenolic Compounds

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**Improved methods of testing for neutral oil and tar acids in phenolic compounds have been worked out in the authors' laboratories on the basis of known blends and pure compounds. The adoption of these improved methods will result in more accurate analysis, the sum of the percentages of neutral oil, tar acids, and water not exceeding 100, as is frequently the case with existing methods. Specifications formulated on the basis of these analytical procedures will represent quality which is at once rigid and dependable.**

**P**HENOLIC compounds or cresylic acids obtained from such sources as petroleum, coal tar, and low- and high-temperature carbonization processes are known to contain varying amounts of neutral oil and tar acids. The neutral oil has been found to be a hydrocarbon mixture of boiling range similar to the acids from which they were extracted, while the acids consist exclusively of phenol, cresols, xylenols, and higher phenolic homologs. Since the amount of neutral oil and tar acids present is a prime consideration in specifications for phenols covering a wide field of industrial usefulness, it is important to determine these constituents with a high degree of accuracy and reproducibility.

### Neutral Oil

The official method for unsaponifiable residue (2) was tried on several samples but without success, the oil being incompletely recovered.

The Standardization of Tar Products Test Committee of London has published a method, Serial No. CC.5-38 (4), for the determination of neutral oil.

The sample is distilled with aqueous sodium hydroxide solution and water, the oil being collected in a graduated separating funnel receiver, the graduated portion of the stem being either 1- or 3-ml. capacity. After allowing for complete separation of oil and water in the receiver, the water is drawn off and the oil volume is read within the graduations and calculated to percentage of the sample.

A method published by Allen (1) also uses steam-distillation, but removes phenols and nitrogen bases from the ether extract of the oil before evaporation and weighing. This method has one possible disadvantage in that some cresylic acids may be lost on evaporation of the ether.

A new method has been developed by the writers which uses a 100-ml. sample and measures the volume of separated oil in a standardized Babcock cream bottle.

**APPARATUS.** Graduated cylinder of 100-ml. capacity. Round short ring-necked flask of 1-liter capacity. Water-cooled condenser.

Balloon separatory funnel of 1-liter capacity. Funnel, 10-cm. (4-inch) size. Small funnel with stem drawn to near capillary size (approximately 1 to 2 mm.).

Babcock bottle, 9-inch, 9-gram, 50 per cent  $\times \frac{1}{2}$ . Beaker of 600-ml. capacity. Burner and shield. Boiling beads and Alundum chips.



**REAGENT.** Sodium hydroxide, 9 to 10 grams per 100 ml.

**PROCEDURE.** One hundred milliliters of sample and 400 ml. of sodium hydroxide are carefully transferred into a 1-liter round short ring-necked flask containing glass beads and Alundum chips. The flask is then fitted to the condenser and the contents are boiled under reflux for 15 minutes, with appropriate flame adjustment to prevent bumping; the flame is then removed and the cresylate solution quickly and cautiously transferred into a 1-liter balloon separatory funnel with the aid of the 10-cm. (4-inch) funnel. That portion of the insoluble material remaining in the flask is rinsed into the separatory funnel with several small portions of the cresylate solution, as drawn from the lower layer in the separatory funnel. (A convenient means of handling the refluxing flask in pouring the cresylate solution is to attach a buret clamp firmly to its neck.)

The solution is then allowed to settle for 30 minutes, permitting the insoluble material to rise to the top. The major portion of the caustic layer is drawn off into a 600-ml. beaker with the exception of a few milliliters, which, together with the insoluble material, are transferred into a 9-inch, 9-gram Babcock bottle. This transfer is made with the aid of a short-stemmed funnel drawn to capillary size for insertion in the neck. The material adhering to the inside walls of the separatory funnel, as well as in the transfer funnel, is washed into the Babcock bottle, using some of the cresylate solution contained in the beaker. The Babcock bottle is then filled, raising the insoluble material within the graduations on the neck.

The sample is then centrifuged at a speed of 1400 r. p. m. for 15 minutes, after which the per cent of insoluble material (neutral oil) is read and reported to the nearest 0.1 per cent.

TABLE I. DETERMINATION OF NEUTRAL OIL

	Method CC.5-38 %	New Method %
Sample 1	2.20	1.0, 1.0
Sample 2	3.04	1.1, 1.1
Sample 3	3.36	1.5, 1.4
Sample 4	0.69	0.1, 0.2
Blend containing 0.5 per cent of oil	..	0.5, 0.5
Blend containing 1.0 per cent of oil	..	0.9, 0.9

Results by this method have repeatedly been obtained with an accuracy of 0.1 per cent on a variety of cresylic acids, and on blends containing known amounts of neutral oil. It has proved very satisfactory as a specification test for quality and as a plant control method. The comparative results shown in Table I have been obtained.

The CC.5-38 method gives high values, because higher boiling nitrogen bases are insoluble in the aqueous layer and thus are collected and measured in the neutral oil. This was proved by subsequent extraction of bases with dilute acid.

### Tar Acids

The method most universally used for the determination of tar acids is that of Chapin (3), called the U. S. D. A. method.

This is performed by distilling 25 ml. of the sample with 75 ml. of kerosene, and collecting the condensate in a Weiss tar-acid separatory funnel. After a treatment with sulfuric acid (1.50 sp. gr.) the volume of treated kerosene solution in the funnel is measured, the cresylic acids are neutralized and extracted with three portions of aqueous sodium hydroxide, and the volume is again measured. The contraction in volume is then multiplied by 4 to obtain the volume percentage of total phenols present.

This procedure has been used in the authors' laboratories for some years, but the results have been inaccurate and usually high for the type of acids tested. These inaccuracies may be accounted for as follows:

When the acids are neutralized with sodium hydroxide solution, they are in intimate contact with kerosene. Since aqueous sodium phenolate will dissolve petroleum fractions to a certain extent, it is very likely that a small amount of kerosene will dissolve in the caustic layer, causing the volume contraction to be abnormally high.

Since the volume of sample used is only 25 ml., any errors in reading are quadrupled in calculating volume per cent of tar acids.

There is a certain amount of mechanical entrainment of kerosene in the caustic solution, and liquid droplets adhere to the

sides of the Weiss funnel after the several extractions have been made, causing certain inaccuracies.

In an effort to remove these difficulties, the authors have worked out a liberation method which yields accurate results on pure acids and commercial phenolic products.

### Liberation Method for Tar Acids

**REAGENTS.** Sodium hydroxide substantially free of carbonate, 200 grams per liter. Sulfuric acid, 25 = 1 per cent by weight. Sulfuric acid, specific gravity at 25° C., 1.50 to 1.51. Petroleum ether.

**APPARATUS.** Pipet, 100-ml., standardized to deliver 100.0 ml. at 25° C. with full drainage; 100-ml. and 250-ml. graduated cylinders; one 500-ml. and two 1-liter pear-shaped separatory funnels. Weiss tar-acid separatory funnel, type 2; 150-ml. and 800-ml. beakers. Small funnel with stem drawn to near capillary size (approximately 1 to 2 mm.).

**PROCEDURE.** Into a 1-liter separatory funnel containing 215 ml. of sodium hydroxide reagent 100 ml. of cresylic acid at 25° C. are pipetted and 100 ml. of petroleum ether are added. (The 100-ml. sample at 25° C. must be transferred quantitatively. A convenient method is to use a portion of the first petroleum ether wash to rinse the pipet with the aid of a small funnel inserted in the pipet.) The funnel is shaken carefully for several minutes, releasing the pressure occasionally. (During the manipulations involved in this determination, care must be taken to make all transfers and extractions quantitatively, rinsing the separatory funnels wherever possible with the solution being used as the wash.) After separation, the cresylate solution is transferred to a second 1-liter separatory funnel and extracted with 50 ml. of petroleum ether. It is shaken for several minutes, separated, and the aqueous layer drained into an 800-ml. beaker.

The petroleum ether extracts are combined and washed twice, first with a 25-ml. portion of sodium hydroxide reagent and then with 25 ml. of water, adding the caustic and water washes to the cresylate solution contained in the beaker.

The beaker and contents are placed on a steam bath under a jet of air for 30 minutes, then placed in a shallow ice bath. After the solution has cooled, it is acidified with constant stirring, using 25 per cent sulfuric acid until a cloud just persists (approximately 125 to 135 ml. should be added). During acidification, the temperature must be kept below 37.78° C. (100° F.).

The cresylate solution is transferred to a 1-liter separatory funnel, using water to rinse the beaker, and 40 ml. of 25 per cent sulfuric acid are added. It is shaken and separation of the liberated tar acids allowed. Then the aqueous layer is drained into another 1-liter separatory funnel and 50 ml. of 25 per cent sulfuric acid are added. The solution is shaken and at least 30 minutes are allowed for the second separation of tar acids.

The tar acids in the first separatory funnel are transferred into a Weiss tar-acid funnel, the aqueous layer is drained back into the first separatory funnel, and the remaining tar acids are extracted with two 50-ml. portions of petroleum ether. In the meantime the tar acids liberated in the second separatory funnel are added to those contained in the Weiss funnel.

The liberated tar acids in the Weiss funnel are now treated with 55 ml. of sulfuric acid (sp. gr. 1.50 to 1.51). In treating the liberated tar acids with sulfuric acid, it is suggested that mixing be secured by inverting the Weiss funnel twelve times. Care must be taken to avoid any loss of tar acids when removing the stoppers from the Weiss funnel.

This first treat is allowed to stand 2 hours, sulfuric acid being drained off at the end of this period. While the first treat is standing, the remaining tar acids extracted by petroleum ether (as outlined in the previous paragraph) are separated from the petroleum ether by 10 ml. of sodium hydroxide reagent, followed by a 10-ml. portion of water. These extracts are combined in a 150-ml. beaker, which is placed upon a steam bath under a jet of air for 30 minutes to remove petroleum ether. The cresylate solution is then cooled in an ice bath and the solution cautiously neutralized with a 50-ml. portion of sulfuric acid (sp. gr. 1.50 to 1.51), using the remainder to wash the liberated tar acids into the Weiss funnel. The tar acids and sulfuric acid now contained in the Weiss funnel are shaken, and allowed to stand 1 hour, the sulfuric acid being drained off at the end of this period.

Another treatment with 25 ml. of sulfuric acid (sp. gr. 1.50 to 1.51) is then given the tar acids, allowing them to stand 30 minutes. During this period the bath is adjusted to a temperature of 25° C. At the end of the settling period the sulfuric acid is drained off and another half hour is allowed for the last traces of sulfuric acid to settle out of the tar acids, after which the per cent of tar acids by volume is finally read at 25° C. and recorded.



Comparative results by the U. S. D. A. and liberation methods on four samples are given in Table II.

TABLE II. DETERMINATION OF TAR ACIDS			
Sample	U. S. D. A. Method	Liberation Method	
	%	%	
1	100.0	97.5, 97.4	
2	101.2	98.3, 98.4	
3	100.4	96.8, 96.8	
4	99.6	97.7, 97.5	

An accuracy of 0.2 per cent is obtainable by the liberation method, as is demonstrated by the foregoing results. As each sample contains both water and neutral oil, the U. S. D. A. values are obviously high, since tar acids alone show 100.0 per cent or more. When per cent of water and neutral oil is added to the liberation method values, the totals are well within 99.5 and 100.0 per cent. The liberation method was

checked using U. S. P. cresol containing 0.2 per cent of water and no neutral oil, the tar acids obtained being 99.8 and 99.9 per cent.

It is firmly believed that the adoption of these improved methods of testing will result in a greater degree of accuracy, and more closely define quality in terms of specification requirements.

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Determining Organic Matter in Paddy Soils  
Reliability of Rapid Titration Methods

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THE volumetric determination of the soil organic matter by measuring the reducing power of the carbonaceous substance with a certain oxidizing solution is generally recognized as being much less laborious than gravimetric methods. In the former case, soils subjected to analysis are digested in a strongly acid solution with a standard solution of either potassium permanganate (2) or chromic acid (4), and the excess of oxidizing agent is then titrated with a reducing solution, frequently oxalic acid or ammonium ferrous sulfate. Previous investigation (1) has shown that results obtained by such methods agree fairly well with gravimetric ones. Owing to their simple and rapid operation, these methods are often employed when a large number of samples is at hand and high accuracy is not desired.

Rapid titration methods, such as those mentioned above, are not at all adaptable for water-logged soils, where high reduction potential usually reduces a part of the oxidizing solution. The presence in these soils of ferrous iron, which is frequently liberated in the boiling solution of strong sulfuric acid, also introduces a serious error into the resulting data.

As the total content of ferrous iron is still not measurable quantitatively, it is rather difficult to distinguish among the portions of the total oxidizing solution consumed by organic matter, ferrous salts, or other reducing substances.

A number of paddy soils have been used as testing samples, and results are given in Table I. The approximate content of ferrous salts in the soils is estimated according to Morgan's method (3).

From the data, it is obvious that erratic results have been yielded most frequently in paddy soils with gleied sub-horizons, which are usually characterized by low organic matter content and relatively high ferrous salt content. These methods are limited in value for such soils.

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TABLE I. ORGANIC MATTER CONTENT OF PADDY SOILS  
(Determined by dry combustion and rapid titration methods)

Samples	Carbon by Dry Combustion Method %	KMnO <sub>4</sub> Method			Chromic Acid Method			Ferrous Salts
		Sample used Gram	Carbon calcd. from result of dry combustion method Mg.	Carbon obtained by KMnO <sub>4</sub> method Mg.	Sample used Gram	Carbon calcd. from result of dry combustion method Mg.	Carbon obtained by CrO <sub>3</sub> method Mg.	
5-8-87 0 to 18 cm.	2.60	0.1546 0.1501	4.02 3.91	4.20 4.25	0.1490 0.1487	3.88 3.88	3.98 3.94	High
18 to 50 cm.	0.55	0.2508 0.2611	1.38 1.43	1.44 1.60	0.2513 0.2544	1.38 1.40	1.58 1.50	Very high
90 to 110 cm.	0.06	0.5043 0.5082	0.30 0.31	1.01 0.84	0.4991 0.5024	6.30 0.30	1.20 1.01	Very high
5-8-80 0 to 20 cm.	0.75	0.1508 0.1611	1.13 1.21	1.25 1.39	0.1513 0.1537	1.13 1.15	1.12 1.28	High
45 to 60 cm.	0.11	0.4981 0.5084	0.55 0.56	1.58 1.81	0.5108 0.4931	0.56 0.54	1.72 1.63	Very high
7-7-6 0 to 20 cm.	0.65	0.2004 0.2087	1.30 1.35	1.61 1.52	0.1945 0.1976	1.29 1.30	1.44 1.60	Very high
20 to 45 cm.	0.09	0.5044 0.5078	0.45 0.46	1.31 1.18	0.5132 0.4958	0.46 0.45	1.40 1.31	Very high



# Colorimetric Evaluation of Derris and Cube Roots

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NUMEROUS qualitative color tests have been proposed for rotenone and other constituents of derris and cube roots, and several quantitative color reactions have been developed for the evaluation of these materials. The purpose of the present study is to review these tests and compare the results obtained by some of these colorimetric methods with each other and with some of the gravimetric methods.

## Review of Color Reactions

Geoffroy (8) was the first to study the color reactions of rotenone with several reagents. The most characteristic of these involved treatment with bromine, followed by application of concentrated sulfuric acid to the residue. A violet color is produced.

One widely used color test is based on the reaction discovered by Durham (9) in which treatment of rotenone with nitric acid followed by ammonia produces an evanescent blue-green color. Ishikawa (14) independently discovered this reaction, using sodium hydroxide as the base. Jones and Smith (17) modified the Durham reaction, using acetone solutions of the unknown and more dilute nitric acid. In this form roughly quantitative estimates can be made. The reaction is also given by deguelin and, with a difference in hue, by toxicarol. Various alkalies may be used to develop the final blue color, and Pozzi-Escot (21) has recently found that even organic bases may be used.

Dennis (6), in a patent on cube, describes a color reaction for testing this material, using sulfuric and nitric acids followed by potassium hydroxide. The directions are not clearly stated, but tests made following the method as closely as possible showed identical color reactions to be given by roots of derris, cube, and *Tephrosia virginiana*.

A useful quantitative color procedure is that devised by Gross and Smith (12) involving treatment of an acetone extract of the sample with alcoholic potassium hydroxide, followed by nitric acid containing sodium nitrite. A fairly permanent red color is given by both deguelin and rotenone. Ambrose and Haag (1) have shortened this test using only the alkali, but in this form the test is not sufficiently specific or delicate. A more serviceable modification is that developed by Goodhue (10), in which the

nitrite is added with the alkali and sulfuric acid is used instead of nitric. This has increased the sensitivity of the original test and the stability of the color.

In 1899 van Sillevoldt (24) found that his "derrid," which undoubtedly contained a high percentage of rotenone, gave a brown-violet color with concentrated sulfuric acid. Danckwortt, Budde, and Baumgarten (5) found that sulfuric acid containing a very small amount of nitrite gives a violet color with rotenone. This suggests that van Sillevoldt's acid contained a trace of nitrite, and Goudswaard and Timmers (11) have recently stated that rotenone may be used as a very sensitive reagent for detecting nitrates and nitrites in sulfuric acid. The sulfuric acid-nitrite reaction was developed into a quantitative test for rotenone by Fischer and Nitsche (7). It has been further modified by Meyer (19), and in this form an aqueous suspension of the material to be tested is treated with the concentrated acid containing the nitrite. The reaction is given by constituents of derris and cube other than rotenone.

Rogers and Calamari (22) have discovered a reaction of rotenone in which the material, when treated with phenol, concentrated hydrochloric acid, and an oxidizing agent, gives a blue to violet color depending on the solvent. They have developed the reaction into a quantitative method using a chloroform or acetone solution of the unknown and thymol and hydrogen peroxide as the oxidizing agent. Light is used to develop the color in the chloroform solution, but in the acetone solution the color develops more rapidly and without the aid of light.

A test for rotenone developed by Pozzi-Escot (20) consists in adding Denigès reagent to a solution of rotenone in concentrated sulfuric acid, obtaining a series of reactions.

Recently Cahn, Phipers, and Boam (4) have suggested a quantitative test for toxicarol involving development of the characteristic phenol color with ferric chloride.

## Comparison of Quantitative Methods

To compare results by some of the quantitative tests, four samples of derris root, three of cube and timbo, and one of *Tephrosia virginiana* were analyzed. (Solomon Love, formerly of this bureau, made some of these analyses.) The results are

TABLE I. COLORIMETRIC AND GRAVIMETRIC ANALYSIS OF DERRIS, CUBE, TIMBO, AND *Tephrosia*

Method of Analysis	Derris								Cube				Timbo		<i>Tephrosia</i>	
	No. 3002 Root <sup>a</sup> %	Extract <sup>b</sup> %	No. 3006 Root %	Extract %	No. 3007 Root %	Extract %	No. 3126 Root %	Extract %	No. 3004 Root %	Extract %	No. 3005 Root %	Extract %	No. 3230 Root %	Extract %	No. 3107 Root %	Extract %
A. Total chloroform extractives	12.6	...	16.5	...	13.6	..	16.7	...	16.4	...	18.4	...	19.2	...	7.8	...
B. Rotenone (by crystallization)	2.0	16	3.6	21	0.6	4	5.8	35	2.9	18	5.6	30	3.9	20	1.4	18
C. Goodhue modification of Gross and Smith test (direct color value)	5.4	43	8.4	51	2.2	16	10.0	60	5.3	32	10.2	55	7.2	38	3.4	44
D. "Deguelin" from color test [(C - B) × 1.25]	4.2	33	6.0	36	2.0	15	5.2	31	3.0	18	5.8	32	4.1	21	2.5	32
E. Dehydro compounds, gravimetric (direct value)	5.1	40	7.8	47	1.3	10	9.1	54	6.0	37	10.7	58	7.3	38	2.0	26
F. "Deguelin" from dehydro compounds (E - B)	3.1	25	4.2	25	0.7	5	3.3	20	3.1	19	5.1	28	3.4	18	0.6	8
G. Meyer (sulfuric acid-nitrite) color test	11.4	90	14.8	90	13.3	98	13.8	83	11.7	71	15.8	86	13.4	70	6.4	82
H. Rogers and Calamari color test <sup>c</sup>	12.5	100	17.5	105	9	65	20	120	23.5	145	26	140	30.5	160	8	100
I. Cahn, Phipers, and Boam (ferric chloride) color test	3.2	25	3.3	20	9.2	68	0.9	5	2.8	17	1.5	8	2.5	13	1.3	17
J. Alkali-soluble material (gravimetric)	3.2	25	3.4	21	9.2	68	1.7	10	4.2	26	2.8	15	5.0	26	1.4	18

<sup>a</sup> Percentages based on root.

<sup>b</sup> Percentages based on extract.

<sup>c</sup> This method appears less precise than the others, and results are not quoted to so many significant figures.



shown in Table I. All extractions were made by the chloroform-room temperature-aliquot method (16), and suitable aliquots were taken. Where necessary the aliquot was evaporated and taken up in other solvents.

Rotenone was determined gravimetrically (*B*) by the method of Jones and Graham (16), and total extractives (*A*) by evaporation of an aliquot of the chloroform extract (18).

Colors obtained by the Goodhue modification (10) of the Gross and Smith method (12) were compared in a neutral wedge photometer using a filter with its optical center at 0.56 micron (*C*). In general, this test is thought to be given principally by rotenone and deguelin in derris and cube. Cahn, Phipers, and Boam (4) state that pure inactive deguelin gives a color value about 80 per cent of that given by rotenone. Therefore, by subtracting from the color value for the samples under study (*C*) the value for rotenone (*B*) and multiplying this difference by 1.25, one arrives at an estimate of the deguelin content (*D*). According to Cahn, Phipers, and Boam (4), this value for ordinary derris roots (such as Nos. 3002, 3006, and 3126) is  $27 \pm 4$  per cent of the extract, and for Sumatra-type roots (such as No. 3007) 9 to 15 per cent. The values obtained in this study are roughly in agreement with this, when one considers that Cahn and his co-workers calculated rotenone from the crude solvate, whereas in this work the slightly lower values for pure rotenone are used, thus making the differences greater in the present work.

The samples were also analyzed by the gravimetric method for rotenone and deguelin originated by Takei, Miyajima, and Ono (25), in which these materials are oxidized to their dehydro derivatives and separated as such, as modified by Tattersfield and Martin (26). To avoid interference from toxicarol, the alkali-soluble material was removed prior to the oxidation. No attempt was made to separate the dehydrorotenone and the dehydrodeguelin as outlined in the original method. The values obtained (*E*) and the differences between these and the rotenone content (*B*), which should represent the deguelin content, are shown in (*F*). The gravimetric values for the derris roots are on the average lower than those by the color method, while for the cube and timbo roots the two methods are in general agreement. The dehydrogenation in the gravimetric procedure may not be entirely quantitative, and the crystallization probably involves a slight loss. This may account for a small part of the difference between the two methods. However, the comparatively large differences for some of the derris roots suggest the possible presence in these samples of a small amount of material giving the red color test but not forming a dehydro compound.

It has not yet been definitely shown that rotenone and deguelin are the only materials in these extracts which give the red color test, or form dehydro compounds in the Takei method. Thus, Buckley (2) and, more recently, Harper (13) have isolated a new compound from derris root which forms a dehydro derivative and, since it gives the Durham test, would be expected to give the red color test, as the two tests are generally given by the same compounds. The values for deguelin by either the colorimetric or the gravimetric method may thus be in error for this reason.

It was shown several years ago (15) that the values by the Gross and Smith color test give a better indication of toxicity of derris and cube samples to insects (houseflies) than does either the rotenone or the total extractives content. Similarly Tattersfield and Martin (26) have found the value for dehydro compounds a good measure of the insecticidal value (to aphids) of derris samples. Thus, whether or not these two methods determine only rotenone and deguelin, they at least are of definite value in giving an approximate indication of toxicity. The color method is simpler and in the Goodhue modification is far more sensitive than the gravimetric pro-

cedure. It is to be hoped that some such method as these, which give a closer approach to insecticidal efficacy than do rotenone or total extractive determinations, will eventually be adopted in the commercial handling of derris and cube roots.

The sulfuric acid-nitrite test (*G*) was made as described by Meyer (19), and comparisons were made with a rotenone standard in a Duboseq type of colorimeter without a filter. Cahn, Phipers, and Boam (4) state that the test is given with equal intensity by rotenone, deguelin, toxicarol, and sumatrol, and by derivatives of these, and that the value for derris extracts is about 90 per cent by this method. It has been learned in a private communication from Dr. Cahn that he used a modification of the Meyer test. For the derris samples in the present work the values averaged about 90 per cent of the extract, but the cube roots gave somewhat lower values.

The Rogers and Calamari test (22) was slightly modified in these analyses. The color in acetone solution was not proportional to the rotenone present, and after a short time solutions of different rotenone concentration developed to about the same color. In chloroform solution the proportionality between color and concentration seemed to hold. Heat as well as light accelerated the color formation, but the latter was adopted. The solutions were exposed in glass cylinders to daylight at the laboratory window (never to direct sunlight) for 24 hours. Perchloric acid was found to effect a more rapid development of the color than the hydrogen peroxide used by Rogers and Calamari. The hue and intensity of the color varied with the amount of perchloric acid used as was the case with other oxidizing agents. At a rotenone concentration of 0.12 mg. per cubic centimeter, 2 drops of 60 per cent perchloric acid gave a moderately intense, pure-blue color in 24 hours. Even in this form results obtained by the test were highly erratic, and duplicate standards (run at the same time) varied as much as 10 per cent. The reaction merits further study, however. Deguelin was found to give a color about 125 per cent of that given by rotenone, whereas toxicarol gave only about one half the color given by rotenone. Since the values obtained on the root samples (*H*), particularly those for the cube and timbo roots, are markedly higher than the total extract values, it is apparent that some constituent in the roots gives a much greater color value than does rotenone or deguelin.

The ferric chloride test for toxicarol and sumatrol (*I*) was made as described by Cahn, Phipers, and Boam (4), and comparisons were made in a Duboseq-type colorimeter. Solutions were compared in pairs, consisting of a standard and an unknown, each pair being prepared fresh. A sample of toxicarol from which as much as possible of the  $\beta$ -toxicarol had been removed, as described by Cahn, Phipers, and Boam (3), was used as a primary standard.

This sample contained 1.5 per cent of  $\beta$ -toxicarol as measured by the Goodhue modification of the Gross and Smith test, in which the color value for  $\beta$ -toxicarol found by Cahn and his co-workers was used. [In spite of this the sample had a melting point of  $217^\circ\text{C}$ . (cor.). Cahn and co-workers state that pure  $\alpha$ -toxicarol (the ordinary form) melts at  $232-3^\circ\text{C}$ . and that material melting at  $219^\circ$  contains 4.5 per cent of the  $\beta$ -isomeride. This matter will be further investigated.] Calculations for the ferric chloride test were made on the assumption that the sample was all  $\alpha$ -toxicarol. Beta-toxicarol has been found to give a color with ferric chloride, but there is some doubt as to the intensity of this color compared with that given by  $\alpha$ -toxicarol. In any event the small amount of  $\beta$ -toxicarol present would not appreciably affect the values obtained on most of the samples. The toxicarol standard was compared with an extract of No. 3007 (a Sumatra-type root), and this in turn was compared with an extract of No. 3006. All other extracts were then compared with



No. 3006. Tests made on only the alkali-soluble portions of some of the extracts gave substantially the same results. In this case it was possible to compare No. 3006 directly with the toxicarol standard, the others again being compared with No. 3006. Some difficulty was encountered in matching the colors from the cube samples, and the use of the alkali-soluble fraction did not improve the color matching. The ferric chloride test indicates from 1.5 to 2.8 per cent of toxicarol and sumatrol in the cube samples, although recently Rowaan and Van Duuren (23) reported that they had been unable to find toxicarol in *Lonchocarpus* (cube) roots. The color may be due to other phenolic compounds.

For comparison the amount of alkali-soluble material was determined by a method previously used (15). This value (J) agrees with the results of the ferric chloride test more closely in the derris roots than in the cube and timbo roots, indicating that in the latter more of the alkali-soluble material is nonphenolic.

### Conclusion

In evaluating derris and cube roots it is now possible—by making use of colorimetric procedures and a determination of rotenone by the usual method to obtain at least approximate values for deguelin and toxicarol—by the Goodhue modification of the Gross and Smith color test to arrive at an estimate of the insecticidal value (for houseflies), and by the Meyer color test to get a rough idea of the total materials of the rotenone type.

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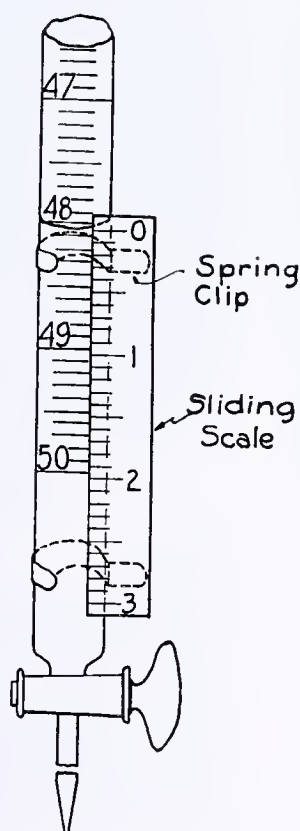
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MANY routine titrations, which require only a relatively small volume of standard solution, may be expedited by taking readings from an attached sliding scale rather than using graduations provided on the buret. Details of the auxiliary scale are shown in the figure.

The slide consists of a small brass strip to which are soldered two brass springs that clip over the buret. Division marks, similar to those on the buret, are made in ink on a piece of white paper glued to the brass strip.

In use the zero mark of the slide is set initially to coincide with the



## An Auxiliary Sliding Scale for Burets

bottom of the meniscus and, after reaching the end point, the titer is read directly from the final reading on the auxiliary scale. By rotating the slide slightly toward the front, the left margin of the divisions will be aligned directly with the axis of the buret and permit better observation of the meniscus.

The use of this device for small titers obviates constant refilling to zero level of buret to eliminate subtractions. Only one numerical reading, the final, need be taken, since the first is always zero. Chance of error in subtractions is thereby avoided.

The device permits extension of usable length of buret beyond graduation limits provided by the manufacturer.

It allows direct conversion of titer into any system of expression without calculation, if the auxiliary slide is specially divided for the purpose. A buret dispensing a single standard solution may be equipped with a number of such sliding scales calibrated for each different application.



# Solubility Characteristics of Tars and Pitches Produced by Coal Hydrogenation

## Determination of Insoluble Matter

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IN THE continuous hydrogenation of coal, the determination of insoluble matter in the products resembling tars and pitches was desirable in calculating hydrogenation yields and as a control test. The necessity of making the determination in a few hours eliminated the Soxhlet extraction methods commonly used in examining coal tar. In the present work the centrifuge was studied as a tool (18, 21, 23) in the rapid determination of insoluble matter. The data obtained give considerable information on the solubility characteristics of heavy oils produced by coal hydrogenation and make possible comparison of coal-hydrogenation and coal-carbonization tars.

### Previous Work

Although no study of the determination of insoluble matter in coal-hydrogenation products has been reported, many methods have been proposed for the estimation of "free carbon" (34, 39) in coal tar.

Kraemer (30) recommended extraction of the tar with forty times its volume of xylene. Köhler (29; 32, p. 240) heated 10 grams of tar with 25 grams of glacial acetic acid and 25 grams of toluene, poured the mixture on two filters of equal weight placed within each other, and washed with hot toluene until colorless. Kraemer and Spilker (31) mixed the tar with 20 parts of xylene, filtered off the insoluble material, washed with 5 parts of xylene, and dried the residue on the filter. The same authors gave another method which involves extracting 1 part of tar with 3 parts of aniline; it was claimed that this method gives 2 to 3 per cent lower results than the xylene method described above, owing to the greater solubility of the tar bitumens in aniline. Ceruti (11) heated 10 grams of tar with 150 cc. of castor oil, filtered, and washed the residue with carbon tetrachloride (41).

Hodurek (24, 25) distinguished between insoluble matter actually suspended in the tar, designated as  $C_1$ , and bituminous material precipitated ( $C_2$ ) by solvents such as benzene. The true "free carbon" ( $C_1$ ) was determined by filtering the tar through fine-grained filter paper;  $C_2$  was estimated by adding benzene to the filtrate. It was stated (24) that bituminous substances ( $C_2$ ) are precipitated by alcohol, benzene, petroleum, toluene, xylene, ether, acetone, and acetic acid, but not by aniline, quinoline, phenol, cresol, nitrobenzene, naphthalene, and anthracene oils.

Hodurek's experiments (24, 25) were repeated and amplified by Berl and Schildwachter (9), who employed tetrahydronaphthalene as a solvent. These investigators recommended use of the latter solvent under pressure for direct determination of suspended insoluble matter,  $C_1$ ; they also demonstrated the importance of the grain of the filtering medium employed in direct filtration of the tar. Adam and Sach (3) concluded that matter insoluble in pyridine (36) corresponds to Hodurek's  $C_1$  and that in toluene or benzene to  $C_1$  plus  $C_2$ . A tar with 22 per cent of free carbon (insoluble in benzene) was found by Evans and Pickard (19) to contain only 14 per cent of pyridine-insoluble material (34).

Solvent	Insoluble, Per Cent		
	Tar	Pitch 1	Pitch 2
Light petroleum			42
Toluene	12.7	26.0	36
Benzene			22
Tetrahydronaphthalene	11.5	20.2	8.5
Cresylic acid	11.0	18.6	..
Aniline	11.7	18.3	..
Pyridine	10.7	16.8	10.5

Simek, Ludmila, and Helm (43) separated benzene-insoluble material (termed alpha-compounds) into fractions soluble and insoluble in anthracene oil (20). The data given above were

TABLE I. FILTRATION AND EXTRACTION OF HORIZONTAL-RETORT TARS

No.	Condition	Filtration Residue %	Insoluble, Per Cent by Weight			
			Carbon bisulfide	Benzene	Acetone	Petroleum ether
8-H	Unfiltered	23.9	5.37	7.92	11.62	18.5
	Filtered		6.52	9.62	14.12	22.5
9-H	Unfiltered	28.9	6.63	11.93	20.8	23.1
	Filtered		8.53	15.36	26.8	29.7

reported by Adam, Shannon, and Sach (4), who determined both the suspended material ( $C_1$ ) and insoluble matter ( $C_1 + C_2$ ) in several tars and pitches.

Marcusson (37) found that the benzene-insoluble components of vertical- and horizontal-retort tars, amounting to 7 and 24 per cent, respectively, consist of oxy-acids (8.6 and 0.5 per cent), pyridine-soluble resins (73 and 16.3 per cent), pyridine-insoluble resins (18.4 and 32 per cent), and partly coked material (0 and 51.2 per cent).

Volkman, Rhodes, and Work (45) determined the suspended matter in 9 tars by filtration and extracted both the filtered and unfiltered tars with carbon bisulfide, benzene, acetone, ethyl ether, and petroleum ether. About the same amounts of insoluble matter were found in both filtered and unfiltered tars; in some instances, the filtration residue exceeded the insoluble matter, as is shown in Table I. Their data, as well as those of other authors (3, 4, 19, 24, 43), show that the amount of insoluble matter found depends largely upon the nature of the solvent.

Mallison (35) and Volkman, Rhodes, and Work (45) state that the yield of "free carbon" depends upon the surface tension of the solvent. Simek, Zamrzla, and Ludmila (44) found that anthracene oil (20) was the best of a number of solvents for alpha-compounds (benzene-insoluble material). It is claimed that, although aniline or pyridine are more effective solvents than benzene and carbon bisulfide, selenium oxychloride (2) has the greatest solvent action.

Hubbard and Reeve (26) compared several methods and proposed the use of cold carbon bisulfide (28; 32, p. 321) as the solvent in estimating free carbon. Objections to this method have been made by Church (12, 13, 14), who prefers extraction with toluene and benzene. Weiss (47, 48) criticized the method of Warnes (46), which involved extraction with 90 per cent benzene and cresylic acid, and proposed the use of the currently well-known toluene-benzene extraction method (6). Bierling (10) used Berl and Schildwachter's method (9) (extraction with 4 volumes of tetrahydronaphthalene at 240° to 250° C. for 2 hours in an autoclave) to determine free carbon. Selvey (42) developed a colorimetric method (2) that involved comparison of stains left on filter papers. Volkman, Rhodes, and Work (45) described an interesting method that requires only traces of tar; the extraction is effected by holding a film of tar on a wire screen in a large volume of mechanically agitated solvent for about 45 minutes.

### Experimental Procedure

Unless otherwise indicated, the following general procedure was used.

Using a balance capable of weighing several hundred grams accurately to 0.01 gram, the weight of a 250-cc. centrifuge bottle was ascertained. After a roll or funnel of ordinary paper had been placed in the mouth of the bottle to direct the tar or oil to the bottom, hot tar was added. The paper funnel was discarded and, after cooling, the bottle and contents were weighed again. To facilitate thorough mixing, the bottle and contents were then heated on a hot plate and the desired amount of solvent, usually 20 volumes, was added slowly, with manual stirring.



After all the solvent had been added, the mixture was stirred mechanically for about 3 minutes. The bottles were then centrifuged at once for 1 hour at about 2400 revolutions per minute. When solvents boiling below 100° C. were used, the supernatant liquid was poured off and the bottle dried several hours at 110° and weighed. For high-boiling solvents, a second wash was made with about 80 volumes of benzene at room temperature; after centrifuging for 0.5 hour the supernatant liquid was removed, and the bottle was dried for several hours at 110° and weighed.

Commercial grades of benzene, tetrahydronaphthalene, and cresol were used. The commercial tetrahydronaphthalene and the 5 per cent cresol-tetrahydronaphthalene solution were analyzed by extraction with 10 per cent sodium hydroxide to determine phenols. Commercial tetrahydronaphthalene (sp. gr., 0.978 at 15.5° C.) contained 2.2 per cent of alkali-soluble material that was assumed to be cresol. The solution prepared by mixing 1 volume of cresol with 19 volumes of commercial tetrahydronaphthalene underwent a volume decrease of 7.3 per cent when extracted with aqueous sodium hydroxide. The tetrahydronaphthalene (sp. gr., 0.973 at 15.5° C.) used in several experiments (Table IX) was purified by extraction with aqueous sodium hydroxide and sulfuric acid, and distillation, the fraction boiling at 205–207° C. being collected.

An independent check of the accuracy of the experiments was obtained from the ash contents of the original heavy oil and of its insoluble matter by the following formula:

$$\text{Per cent insoluble matter} = \frac{\text{per cent ash in tar (100)}}{\text{per cent ash in insoluble matter}}$$

The "free-carbon" values calculated in this manner are given below with the determined values for comparison. The agreement is usually satisfactory.

The tars and heavy oils used in the present work are described in Table II. Sample 1, Table II, which was used in most of the experiments, was a viscous oil discharged from the bottom of the converter during the continuous hydrogenation (22) of coal. Although it had been centrifuged, it contained 3.76 per cent of ash. It is likely that only negligible amounts of the remaining insoluble matter settled out during the several months consumed in collecting data. The pastes described in Table II were prepared by mixing the heavy oils from previous hydrogenations (22) with a little less than an equal amount of pulverized (200-mesh) coal.

TABLE II. PROPERTIES OF TARS, HEAVY OILS, AND PASTES

Source	No.	H	C	N	O	S	Ash	Sp. Gr. at 15.6° C.
Per cent by weight								
Coal hydrogenation	1	6.62	86.16	1.25	1.79	0.42	3.76	1.173
	2	...	...	...	...	...	6.70	...
	3	...	...	...	...	...	7.00	...
	4	...	...	...	...	...	7.52	...
	5	...	...	...	...	...	6.61	...
Coal carbonization	6	5.63	91.09	1.02	1.44	0.76	0.06	1.165
	7	5.46	92.37	1.15	0.54	0.45	0.03	1.207
	8	5.8	90.9	1.1	1.6	0.6	...	...
	9	5.8	91.0	1.1	1.5	0.6	...	...
	10	5.4	91.2	1.1	1.8	0.5	...	...
	11	5.4	91.1	1.2	1.9	0.4	...	...
Coal- hydrogenation paste	12	...	...	...	...	...	5.10	...
	13	...	...	...	...	...	5.50	...
	14	...	...	...	...	...	4.55	...

### Effect of Solvent

It was found that heavy oil (sample 1, Table II) produced by coal hydrogenation has solubility characteristics generally similar to those of tars and pitches produced by coal carbonization. Table III gives the data obtained when 1 part of heavy oil was washed once with 20 volumes of low-boiling solvent. The results obtained by one wash with 20 volumes of high-boiling solvent, followed by one wash with about 80 volumes of benzene, are given in Table IV. The ratio of

TABLE III. COMPARISON OF LOW-BOILING SOLVENTS

Solvent	Surface Tension at 20° C. <sup>a</sup>	Insoluble, Per Cent by Weight	
		Found	Calculated
Ethanol	22.27	69.09 <sup>b</sup>	...
Heptane	About 20	67.59 <sup>b</sup>	...
Ether	17.10	37.38	37.50
Acetone	23.7	32.10	32.20
Ethyl acetate	23.9	32.05	31.72
Benzene	28.28	28.24	27.90

<sup>a</sup> (27). <sup>b</sup> Fused on drying at 110° C.

TABLE IV. COMPARISON OF HIGH-BOILING SOLVENTS

Solvent	Surface Tension at 20° C.	Insoluble, Per Cent by Weight	
		Found	Calculated
Decahydronaphthalene <sup>a</sup>	26.7 (15.5°)	28.24	28.42
Diphenyl ether <sup>a</sup>	...	22.20	21.89
Tetrahydronaphthalene <sup>a</sup>	34.3	20.03	20.03
	34.3	17.40	17.62
	34.3 <sup>b</sup>	17.45 <sup>b</sup>	17.37 <sup>b</sup>
Furfural <sup>a</sup>	43.5	12.90	13.32
Aniline <sup>b</sup>	42.58	10.77	11.17
Nitrobenzene <sup>b</sup>	43.38	8.93	9.82
Pyridine <sup>a</sup>	38.0	8.85	9.27
Cresol <sup>b</sup>	37	8.67	9.28
Quinoline <sup>b</sup>	45.0	7.41	9.46

<sup>a</sup> Solvent at room temperature.

<sup>b</sup> Solvent at about 90° C.

solvent to heavy oil was selected on the basis of Figure 1; it does not necessarily follow that 20 volumes is the optimum ratio for each of the solvents. Moreover, the results shown in Table IV probably do not represent the solvent powers of the high-boiling solvents exactly because of the second wash with benzene.

The results in Tables III and IV, which range from 8 to 69 per cent insoluble matter, agree generally with data previously reported on coal tars and show that polar solvents give lowest values for "free carbon." In agreement with previous statements (35, 45), there is a rough correlation between surface tension and solvent power. However, this generalization obviously cannot be extended to include solvents such as glycol, glycerol, and water, which, although having high surface tensions, are poor solvents for tars and pitches.

### Effect of Ratio of Solvent to Sample

Although the effect of the ratio of solvent to the tar sample has not been investigated thoroughly, 3 to 100 volumes of solvent are usually recommended. An interesting study (45) was made recently of the effect of solvent ratio for very large amounts of solvent (200 to 7100 volumes). The results showed that the solvent ratio is important; as a result of this work, concentrations above 200 mg. of sample per 100 cc. of solvent (ratio of solvent to sample, less than 500) were recommended.

The ratio of solvent to sample was found to be important for heavy oil produced by coal hydrogenation (Tables V to VII). The effect of solvent ratio for three solvents (benzene, tetrahydronaphthalene, and cresol-tetrahydronaphthalene solution) was studied for ratios up to about 40, using the centrifuge-bottle method described above. The wire-screen method of Volkmann, Rhodes, and Work (45) was employed with benzene (Table V) to determine the effect of higher solvent ratios (430 to 2000 volumes).

With all three solvents, the amount extracted increased rapidly at first with increase in solvent ratio and then more slowly (Figures 1 and 2). The stage at which further increases in solvent ratio are relatively unimportant varied with the efficiency of the solvent. For benzene, tetrahydronaphthalene, and cresol-tetrahydronaphthalene solution, these approximate values are 20, 14, and 10 volumes of solvent,



TABLE V. EFFECT OF RATIO OF SOLVENT (BENZENE) TO HEAVY OIL

Ratio of Solvent to Heavy Oil	Insoluble, Per Cent by Weight Found	Calculated
5	38.32	...
10	34.51	32.65
15	31.64	30.75
20	28.24	27.90
25	29.15	28.00
26	28.16	27.72
27	27.53	27.29
30	27.77	27.15
32	26.78	26.12
34	26.90	26.10
37	27.14	27.00
39	27.66	26.61
430 <sup>a</sup>	21.35	...
630 <sup>a</sup>	19.27	...
1155 <sup>a</sup>	19.27	...
1400 <sup>a</sup>	20.02	...
1600 <sup>a</sup>	20.84	...
2000 <sup>a</sup>	20.18	...

<sup>a</sup> Determined by wire-screen method (45).

TABLE VI. EFFECT OF RATIO OF SOLVENT (TETRAHYDRO-NAPHTHALENE) TO HEAVY OIL

Ratio of Solvent to Heavy Oil	Insoluble, Per Cent by Weight Found	Calculated
4	29.47	...
6	24.53	...
8	21.59	...
10.6	19.45	19.25
12	19.28	19.33
14	18.11	18.32
16	17.76	17.95
17.2	17.94	17.88
20	17.45	17.37
25	17.07	17.05
30	17.23	17.37
33	17.74	17.85

TABLE VII. EFFECT OF RATIO OF SOLVENT (CRESOL-TETRA-HYDRONAPHTHALENE) TO HEAVY OIL

Ratio of Solvent <sup>a</sup> to Heavy Oil	Insoluble, Per Cent by Weight Found	Calculated
4	19.15	16.98
6	16.79	16.65
10	14.73	15.09
16.1	14.65	14.78
18.7	14.75	14.95
20	14.32	14.77
21	14.42	15.15
25	14.19	14.67
30	13.89	14.37

<sup>a</sup> Contained 7.3 per cent (volume) of cresol.

respectively. These facts are important in devising analytical methods, since it should be easier to get consistent results by using solvent ratios above the threshold values mentioned above. It is noteworthy that well-known methods (6, 7) of determining insoluble matter employ large amounts of solvent.

The data obtained with benzene by the centrifuge-bottle method (5 to 39 volumes of solvent) and by the wire-screen method (430 to 2000 volumes) are plotted together in Figure 2, although these two sets of data are not exactly comparable. The data on acetone reported by Volk-mann, Rhodes, and Work (45) give a similar curve when plotted in this fashion. Figure 2 shows that the amount extracted increases rapidly with solvent ratio to about 20, slowly from 20 to about 500, and little or none above 500 volumes of solvent.

The data obtained with low solvent ratios (4 to 18), which appear on decidedly curved lines in Figures 1 and 2, gave approximately straight lines when the concentration of tar in solvent, instead of solvent ratio, was plotted against insoluble matter (Figure 3). These straight lines, whose slopes decrease with increase in extraction efficiency of the solvent, might be useful for pre-dicting solubility by interpolation or extra-

polation when low solvents ratios are used. Figures 1 and 2 should be more useful for predicting solubility in large amounts of solvent. The straight lines of Figure 3 cannot be extrapolated to zero concentration to find the solubility of tar in extremely large volumes of solvent because, as has been demonstrated with acetone (45) and benzene (Figure 2), solubility is not even approximately a straight-line function of the concentration for concentrations lower than about 0.2 gram per 100 cc. of solvent. However, the values obtained by extrapolation to zero concentration might be useful for comparative purposes.

Extraction with Mixtures of Polar and Nonpolar Solvents

It was observed that the amount extracted with a solution of polar and nonpolar liquids cannot be predicted by the mixture law—that is, the amount extracted is not a straight-line function of the composition of the solvent (Tables VIII and IX, and Figure 4). The components of the two solutions studied in this connection are (a) benzene and pyridine and (b) tetrahydronaphthalene and cresol, all characteristic of coal-tar distillates. The amount extracted increased rapidly at first, then slowly as the concentration of the polar solvent component increased (Figure 4). These data show that the solvent power of coal-tar distillates is enhanced far more by tar acids and bases than would be expected from their con-centration.

TABLE VIII. EXTRACTION WITH BENZENE-PYRIDINE SOLUTIONS

Solvent		Insoluble, Per Cent by Weight	
Benzene %	Pyridine %	Found	Calculated
100	0	28.24	27.90
95	5	22.62	21.49
90	10	19.41	18.32
80	20	16.69	16.25
0	100	8.85	9.27

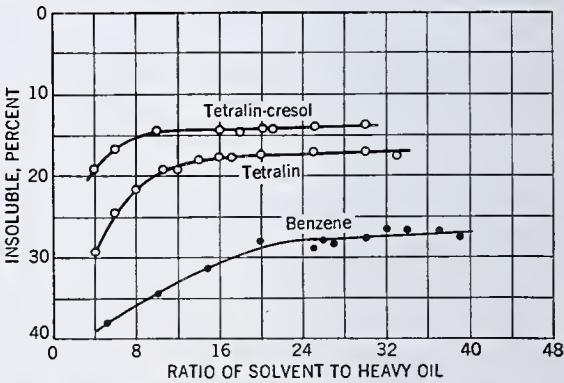


FIGURE 1. EFFECT OF RATIO OF SOLVENT TO HEAVY OIL

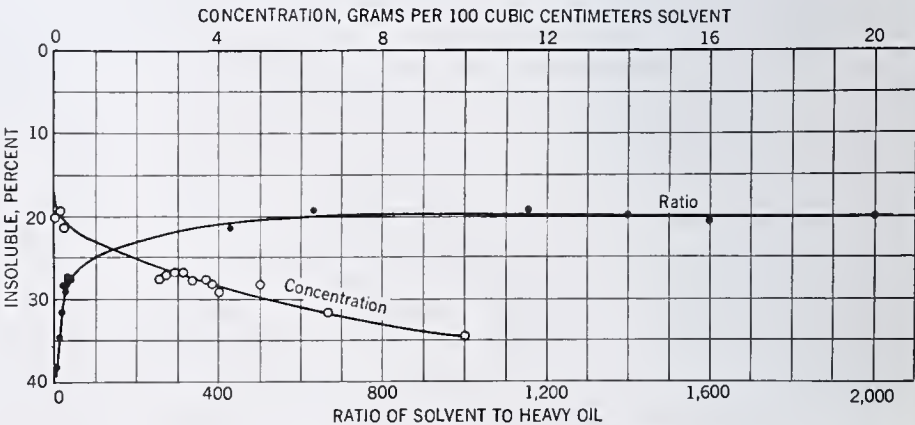


FIGURE 2. EXTRACTION OF HEAVY OIL WITH BENZENE



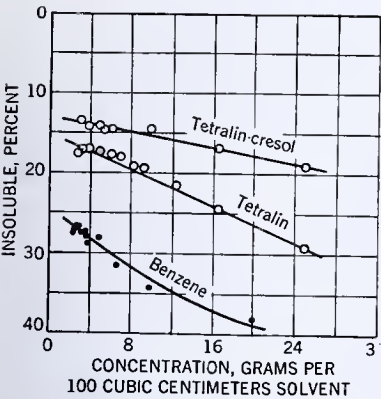


FIGURE 3. EFFECT OF CONCENTRATION OF HEAVY OIL IN SOLVENT

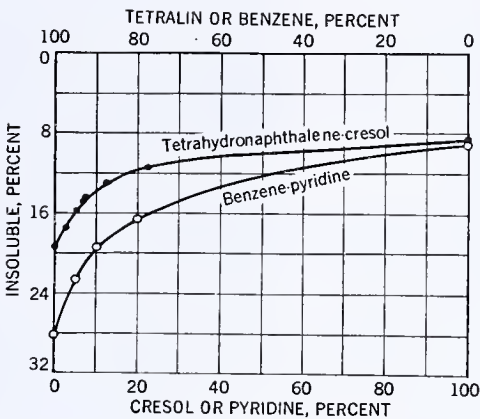


FIGURE 4. EXTRACTION OF HEAVY OIL WITH BINARY SOLUTIONS

Table IX also contains data obtained with other tetrahydronaphthalene solutions. Since naphthalene is a probable impurity in commercial tetrahydronaphthalene, the solubility of the heavy oil in several naphthalene-tetrahydronaphthalene solutions was determined. It was found that the solubility characteristics of tetrahydronaphthalene are affected very little by the addition of as much as 10 per cent of naphthalene. On the other hand, the addition of the cresols to tetrahydronaphthalene increased the solvent power considerably, *p*-cresol being more effective than *o*-cresol. The addition of phenol to tetrahydronaphthalene also gave a more effective solvent. From these results it can be concluded that tetrahydronaphthalene-cresol solutions should give reproducible results if the tar-acid content, which can be determined easily by extraction with sodium hydroxide solution, is kept constant.

TABLE IX. EXTRACTION WITH TETRAHYDRONAPHTHALENE SOLUTIONS

Tetrahydro-naphthalene %	Solvent Other component %	Insoluble, Per Cent by Weight Found	Insoluble, Per Cent by Weight Calculated
100 <sup>a</sup>	.....	19.35	19.40
97.7	Tar acids, 2.3	17.45	17.37
95 <sup>a</sup>	Cresol, 5	{ 15.77	15.56
		{ 15.74	15.72
93 <sup>a</sup>	Cresol, 7	14.81	14.59
92.7	Cresol, 7.3	14.32	14.77
87.7	Cresol, 12.3	12.89	13.32
77.7	Cresol, 22.3	11.54	11.88
0	Cresol, 100	8.67	9.28
92.7	Cresol, 7.3	14.60 <sup>b</sup>	14.95 <sup>b</sup>
97.5 <sup>a</sup>	Naphthalene, 2.5	19.02	18.75
95 <sup>a</sup>	Naphthalene, 5	20.30	19.95
90 <sup>a</sup>	Naphthalene, 10	19.79	19.38
95	<i>o</i> -Cresol, 5	15.23	15.27
95	<i>p</i> -Cresol, 5	13.82	14.23
93 <sup>a</sup>	Phenol, 7	14.37	14.30

<sup>a</sup> Solution prepared from purified tetrahydronaphthalene.  
<sup>b</sup> Hot tar treated with cold solvent (room temperature).

Effect of Preheating

Preheating the heavy oil at moderate temperatures had little effect on the determination of insoluble matter. When the standard heavy oil (No. 1, Table II) was heated in a centrifuge bottle at 105° to 110° C. for 20 hours the loss in weight was 2.06 per cent. However, the amount of insoluble matter found in the nonvolatile residue was 14.62 per cent (calculated value, 14.84 per cent) of the original sample. This value compares favorably with the result (14.32 per cent, Table VII) obtained in the usual manner.

This result might have been predicted from the results of Simek, Zamrzla, and Ludmila (44), who studied the rate of formation of material insoluble in benzene (alpha-compounds) from those soluble therein (beta- and gamma-compounds). The formation of alpha-compounds proceeded

slowly at 350° (4.95 per cent in 60 minutes, 10.91 per cent in 600 minutes). Although the formation of alpha-compounds began slowly at 450° (6.85 per cent in 60 minutes), it was markedly accelerated after the first hour (38.58 per cent in 120 minutes). Reeve (40) increased the "free-carbon" content by heating the tar at about 400° for 5 hours under a pressure of 6 to 7 atmospheres.

Effect of Temperature

The effect of temperature over a small range is illustrated by some of the data in Tables IV and IX. The experiments with tetrahydronaphthalene and 5 per cent cresol-tetrahydronaphthalene solution were made as follows: At the higher temperature, 20

volumes of hot solvent (90° to 100° C.) were stirred into the hot heavy oil, and the resulting mixture was stirred mechanically for about 3 minutes. At the lower temperature 20 volumes of solvent (room temperature) were stirred into the hot heavy oil. The resulting mixture, at a temperature of about 45°, was then stirred mechanically for about 3 minutes. There was very little difference in the results obtained by these two methods. However, when the hot, heavy oil was cooled quickly by rapid addition of cold solvent thorough mixing was hindered, and a higher value (20.03 instead of 17.4 per cent) resulted (Table IV).

Table X gives results obtained with several oils that were moderately fluid at room temperature. These results should be more significant since, in contrast with the more viscous samples, it was comparatively easy to mix sample and solvent at room temperature. The room-temperature determinations of Table X were made by adding 20 volumes of 5 per cent cresol-tetrahydronaphthalene solution to the fluid oil without previously heating either solvent or sample. Both sample and solvent were preheated to 90° to 100° C. for the high-temperature determinations. Table X shows that, with one exception, higher values for insoluble matter were obtained at room temperature. In agreement with previous work (45), it appears that small differences in temperature have little effect on the amount of insoluble matter.

Miscellaneous Variables

That continued washing is desirable under some conditions of extraction is evidenced by the fact that "free carbon" usually is determined by continuous extraction (6) in Soxhlet apparatus. Nevertheless, it is possible to avoid this time-consuming operation by working under proper conditions. Table XI shows that when 20 volumes of tetrahydronaphthalene are used most of the material soluble in tetrahydro-

TABLE X. EFFECT OF TEMPERATURE

Insoluble, Per Cent	
Room temperature	90° to 100° C.
5.79	4.74
7.00	5.42
7.09	5.49
4.76	4.76

TABLE XI. EFFECT OF REPEATED WASHING

Tetralin Washes	Benzene Washes	Insoluble, Per Cent by Weight	
1	1	17.45	17.37
2	1	14.88	15.50
2	1	15.45	16.21
2	2	15.26	16.03
1	2	15.71	16.52
1	2	15.90	16.61
1	3	16.24	16.89



naphthalene or benzene is removed in the first wash. This indicates that one or, at the most, two washings under these conditions suffice to remove virtually all the tetrahydronaphthalene-soluble material and that this method, either with tetrahydronaphthalene or a similar solvent, can be used satisfactorily as the basis of an analytical method.

Stirring the heavy oil (No. 1, Table II) with 20 volumes of 5 per cent cresol-tetrahydronaphthalene solution for 15 minutes instead of 3 minutes (the standard time) had little effect. The results found after 15 and 3 minutes of mechanical stirring are 14.52 and 14.32 per cent, respectively. The corresponding values calculated from the ash contents are 14.65 and 14.77 per cent; therefore continued stirring is not necessary and has little effect upon the results.

As has been observed previously with other methods (23, 33, 38), the insoluble matter was found to increase slowly with time of contact with the solvent. Heavy oil 1, Table II, gave 14.32 per cent insoluble matter by the standard method in which the sample is in contact with 20 volumes of the solvent for 1 hour or less. When the heavy oil was allowed to remain in contact with the solvent (after 3 minutes of stirring but before centrifuging) for 17, 241, and 386 hours the values obtained for insoluble matter are 15.26, 17.66, and 18.67 per cent, respectively. The corresponding values calculated from the ash contents are 15.57, 17.87, and 18.71 per cent. Consequently, the mixture should be centrifuged immediately after the stirring operation to get consistent results. It is claimed that the insoluble matter reaches maximum value after standing with the solvent for about 120 hours (33).

Previous workers (5, 15) showed that light causes matter to precipitate from carbon tetrachloride (41) solutions of bitumens. The amount precipitated in control experiments was considerably less, although there was some precipitation on standing in the absence of light. It was not considered necessary to study this variable in the present work, since in any analytical procedure that would be adopted the solution would be exposed to light for only a few minutes before centrifuging.

Table XII shows that centrifuging for 10 or 15 minutes will separate the 5 per cent cresol-tetrahydronaphthalene solution from the insoluble matter. Corresponding experiments for the second wash with benzene were not made, but less centrifuging should be required for benzene (sp. gr., 0.879) than for the cresol-tetrahydronaphthalene solution (sp. gr., 0.980).

TABLE XII. EFFECT OF CENTRIFUGING ON INSOLUBLE MATTER DETERMINATION

Centrifuging Time Min.	Insoluble, Per Cent by Weight Found	Calculated from ash content
10	14.18	14.55
15	14.03	14.42
30	14.33	14.65
45	14.67	14.95
60	14.32	14.77

### Method Adopted

From the foregoing account it is evident that the amount of insoluble matter depends almost entirely upon the analytical method used and that methods can be devised to give almost any desired answer. Since there is considerable latitude in choice of solvent, solvent ratio, and other conditions, it remains only to select a method that has the particular features desired for the problems at hand.

The following procedure appeared most suitable for the authors' purpose for several reasons that are here stated.

About 10 grams of sample are weighed into a 250-cc. centrifuge bottle and heated to about 90° C. Twenty volumes of 7 per cent cresol-tetrahydronaphthalene solution (previously heated to about 90° C.) are added slowly, with manual stirring. The resulting mixture is stirred mechanically for approximately 3 minutes and then centrifuged at about 2400 r. p. m. for about 20 minutes. The supernatant layer is decanted and 150 to 200 cc. of benzene (room temperature) are added. The solid residue is broken with a stirring rod, after which the mixture is stirred mechanically for about 3 minutes and centrifuged. The layer of benzene is decanted, after which the bottle and residue are dried to constant weight at 110° C. (2 or 3 hours).

This method is rapid, final results being obtainable in about 3 or 4 hours. The solvent power of the solvent (7 per cent cresol in tetrahydronaphthalene) should approximate that of tar and hydrogenated coal distillates. Enough solvent (20 volumes) is used to dissolve virtually all the reasonably soluble components. Since approximately the same results are obtained with 18 to 22 volumes of solvent, it is unnecessary to measure the solvent used with great accuracy.

TABLE XIII. INSOLUBLE MATTER IN TARS AND PITCHES DETERMINED BY DIFFERENT METHODS

No. (Table II)		(Per Cent by Weight)			
		A	B	C	D
1	Heavy oil	14.32	...	17.2	18.19
2	Heavy oil	11.94	...	13.0	...
3	Heavy oil	15.66	...	13.3	...
4	Heavy oil	13.39	12.67	16.1	...
5	Heavy oil	13.99	...	...	16.25
	Coal-hydrogenation converter drainage	18.71	18.55	...	...
12	Coal-hydrogenation paste	43.70	...	40.9	...
12	Coal-hydrogenation paste	42.81 <sup>b</sup>	40.35	40.9	...
13	Coal-hydrogenation paste	45.87	...	43.4	...
13	Coal-hydrogenation paste	44.31 <sup>b</sup>	41.60	43.4	...
14	Coal-hydrogenation paste	45.75	45.25	45.70	...
	Coal tar	2.02	...	...	4.61
		2.02	...	...	4.34
		4.09	...	...	6.47
		4.57	...	...	7.74
		8.73	...	...	8.58
		3.61	...	...	4.00

<sup>a</sup> Methods are:

A = Adopted method using centrifuge.

B = A plus Soxhlet extraction with benzene.

C = Two washes with 5 volumes of tetrahydronaphthalene, two washes with benzene, and Soxhlet extraction with benzene.

D = Gas Chemist's Handbook method.

<sup>b</sup> Extracted twice instead of once with benzene.

Enough residue is obtained from coal hydrogenation pitches for determination of moisture, ash, etc. From the ash contents of the residue and the original sample, the percentage of insoluble matter can be calculated to check the determined value. By employing a six-place head for the centrifuge, six determinations can be made easily at one time. The efficacy of the solvent depends primarily upon the cresol content, which is easily determined by extraction with sodium hydroxide solution. The solvent is thermally stable and can be recovered by simple distillation. The residues obtained are such that the centrifuge bottles can be cleaned easily. Most tars and many pitches are fluid at 90° to 100° C. and hence easily mixed with solvent at the temperature employed. Presumably, high-melting pitches could be examined by this method after being finely pulverized.

The new method gives results somewhat lower (Table XIII) than those obtained by the well-known "free-carbon" determination (6), in which the sample is extracted with benzene in Soxhlet apparatus after a preliminary wash with warm toluene. Several of the residues obtained by the new method were extracted for 48 hours with benzene in Soxhlet apparatus. The results (column B in Table XIII) show that small percentages of the residues are extractable with hot benzene.

The reproducibility of the method is shown by Table XIV. The determined values check each other better than the values calculated from the ash content, but in nearly all instances the agreement is satisfactory.



TABLE XIV. DUPLICATE DETERMINATIONS<sup>a</sup>

Insoluble Matter, Per Cent		
Found		Calculated from ash content
45.75	45.76	45.70
4.82	4.79	4.95
11.95	11.99 <sup>b</sup>	12.15
4.82	4.79	4.95
11.77	11.84	12.08
13.37	13.42	13.70
18.69	18.73	19.29
8.75	8.56	...
49.95	49.15	51.10
55.33	55.20	55.70
32.04	32.06	32.27
9.57	9.64	9.41
17.06	16.97	17.42
54.94	54.98	54.90
55.94	56.08	55.90
17.45	17.49	17.73
60.85	60.88	60.80
43.44	43.95	43.85
20.98	21.04	21.15
21.74	21.78	22.00

<sup>a</sup> Samples are heavy oils, pitches, pasting oils, and centrifuge residues produced or used in coal hydrogenation.

<sup>b</sup> A third determination gave 11.87 per cent of insoluble matter.

### Composition of Insoluble Matter

Ultimate analyses were made of the insoluble matter found in several heavy oils produced by hydrogenating coal and coal tar. As is to be expected, these insoluble products contain much ash and carbon and little hydrogen (Tables XV and XVI). Probably the precursors of most of the insoluble matter in the products of coal hydrogenation are the fusain and opaque attritus of the original coal. Both fusain and opaque attritus have high carbon-hydrogen ratios and are difficult to liquefy by hydrogenation.

For the purpose of comparison, the composition of free carbon (34) from coal tars may be considered. Hubbard and Reeve (26) analyzed several samples of free carbon and reported the following data:

Carbon	90.17 to 94.26
Hydrogen	2.59 to 3.31
Oxygen	1.81 to 5.91
Sulfur	0.50 to 1.78
Nitrogen	No trace upon qualitative test

The results of Hubbard and Reeve are roughly similar to those found by other investigators, except that considerable amounts of nitrogen are usually found (Table XVI). Mallison (35) gave the following as the composition of free carbon: C, 90.0 to 91.7; H, 3.4 to 4.0; N, 1.0 to 1.2; S, 0.7 to 1.4; and O, 2.5 to 3.3 per cent. Table XVI gives the ultimate analyses of other samples of free carbon obtained from coal tar by solvent extraction. All these samples of insoluble matter are characterized by high carbon and low hydrogen contents. From the data in Table XVI the insoluble matter from coal-hydrogenation products appears to have higher hydrogen contents and lower carbon-hydrogen ratios than that occurring in tars produced by the carbonization of coal. Since the insoluble residues (Table XVI) from coal-hydrogenation products contain 15 to 30 per cent of ash, the data calculated to the dry, ash-free basis may not represent exactly the insoluble organic matter. Insoluble matter from carbonization tars contains only traces of mineral matter, and hence their ultimate analyses are more significant.

Unpublished results obtained at the Bureau of Mines during the continuous hydrogenation of high-temperature coal tar are interesting in connection with the nature of the "free carbon" or insoluble matter. Although the tar contained nearly 9 per cent of "free carbon" (as determined by benzene extraction in Soxhlet apparatus and the cresol-tetrahydro-naphthalene method described above), the insoluble matter content of the product discharged from the bottom of the hydrogenation converter remained constant at about 1.5 per

cent. This indicates that continuous hydrogenation, in which the heavy products are recycled, converts all the tar into liquid, gaseous, or soluble products. Therefore, the "free carbon" of this tar, although of high carbon content and molecular weight, is not inert and is considerably different from carbon, charcoal, fusain, etc. One sample of "free carbon" from coal tar was found to have a molecular weight of 2000 in anthracene (16).

TABLE XV. ANALYSIS OF INSOLUBLE MATTER IN HEAVY OIL FROM HYDROGENATION OF COAL AND COAL TAR (DRY BASIS)

Volatiles	Fixed Carbon	Ash	H	C	N	O	S
Proximate, per cent			Ultimate, per cent				
14.60	55.55	29.85	3.05	60.49	0.98	2.91	2.72
20.20	63.78	16.02	3.96	72.80	1.33	4.41	1.48
16.75	57.79	25.46	3.46	63.86	1.08	3.83	2.31
14.70	70.54	14.76	3.60	75.30	1.55	3.36	1.43
15.75	66.85	17.40	3.53	73.07	1.41	2.79	1.80
14.60	65.02	20.38	3.42	69.63	1.28	3.50	1.79
15.90	61.59	22.51	3.37	68.14	1.18	2.99	1.81
10.4 <sup>a</sup>	75.7	13.9	2.3	79.4	0.8	0.7	2.9
... <sup>a</sup>	...	9.3	2.6	80.3	1.4	4.9	1.5
... <sup>b</sup>	...	2.4	3.8	83.0	2.2	7.8	0.8

<sup>a</sup> Heavy oil from hydrogenation of coal tar.

<sup>b</sup> Coal tar.

TABLE XVI. ANALYSIS OF INSOLUBLE MATTER IN TARS, PITCHES, ETC.

Source	(Dry, ash-free basis)					C/H Ratio	Reference
	H	C	N	O	S		
	<i>Per cent by weight</i>						
Heavy oil <sup>a</sup>	4.3	89.2	1.4	4.4	<i>b</i>	20.8	(22)
	4.7	88.3	1.6	4.7	<i>b</i>	18.8	(22)
	4.7	88.4	1.4	4.8	<i>b</i>	18.8	(22)
	4.2	89.9	1.9	3.3	<i>b</i>	21.4	(22)
	4.3	90.4	1.7	2.9	<i>b</i>	21.0	(22)
	4.3	89.3	1.6	4.1	<i>b</i>	20.8	(22)
	4.4	89.9	1.6	3.4	<i>b</i>	20.4	(22)
Heavy oil <sup>c</sup>	2.7	94.5	1.0	1.1	<i>b</i>	35.0	...
	2.9	89.5	1.6	5.3	<i>b</i>	30.9	...
Coal tar	3.9	85.2	2.3	7.9	<i>b</i>	21.8	...
	2.3	89.8	0.7	7.2	..	39.1	(17)
	3.1	91.2	...	...	..	29.4	(8; 32, Part 1, p. 431)
	3.2	92.7	...	...	..	29.0	(8; 32, Part 1, p. 431)
	3.3	91.1	1.1	3.2	1.3	27.6	(43)
	2.79	90.0	...	...	..	32.3	(3)

<sup>a</sup> Produced by coal hydrogenation (22).

<sup>b</sup> Organic sulfur assumed to be 0.7 per cent (1).

<sup>c</sup> Produced by hydrogenation of coal tar.

### Acknowledgment

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## Determination of Phenols in Hydrocarbon Solvents

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IT IS well known that the presence of phenolic compounds in oleoresinous compositions tends to retard the drying rate. Certain hydrocarbon solvents have been shown to have an adverse effect on drying, due to the presence of small amounts of phenolic bodies. Since no adequate analytical method for the determination of small amounts of phenols in hydrocarbon solvents has ever been published, this work was undertaken with a view to establishing a method of controlling the phenol content of solvents used for paints.

Petroleum solvents may differ considerably in their phenolic content, depending on the source of supply and the methods of manufacture and purification. Since the major portion of the phenolic contaminants is removed at the refinery, any useful method of isolation and determination must be applicable to amounts on the order of 10 to 100 parts of the phenol per million.

Most quantitative methods suffer from the disadvantage of being inapplicable either to substituted phenols which are present in the highly aromatic type of solvents being considered or to phenols which are not effective reducing agents. Volumetric methods, such as the familiar bromate-bromide method, are essentially macro methods and insufficiently accurate for estimation of contaminants. Among the available colorimetric methods, those of Folin and Denis (1) and of Gibbs (2) have received the most attention. The former is based on reduction of phosphomolybdic-phosphotungstic acid presumably to lower oxides of molybdenum and tungsten, resulting in formation of deep blue colored solutions. It has been found specially suitable for the estimation of aminophenols and polyhydroxy phenols which are strong reducing

agents, but the reagent is less satisfactory for the estimation of the higher alkyl substituted phenols which are found in high-solvency petroleum solvents. The Gibbs method, which is based on indophenol dyestuff formation by reaction of phenols with 2,6-dibromoquinone chloroimide, is inapplicable to para-substituted phenols; in fact, even with the para position unsubstituted some phenols have failed to undergo reaction.

The procedure herein described is particularly suitable for the colorimetric estimation of the higher alkyl substituted phenols in petroleum solvents, which are only slightly soluble or insoluble in water. A method similar in principle and as applied to certain biological materials has been described by Stoughton (3).

In the present method, the phenolic bodies are separated from the hydrocarbon solvent by successive extractions with dilute aqueous alkali until the extract is phenol-free, as indicated by a negative phenol test on the final extract. Since the alkali salts of the higher alkyl substituted phenols have a limited solubility in water due to their high molecular weight, repeated extractions are essential; alkali-insoluble phenols containing 8 carbon atoms or more in the side chains are usually not encountered, because of their high boiling point, and are not apt to appear in solvents suitable for the paint and varnish industry. Steam-distillation is an ineffective means of isolation of the phenol contaminants because of the high volatility of the hydrocarbon solvent.

After extraction, an aliquot of the alkaline phenol solution is neutralized, then diluted with an equal volume of glacial acetic acid to liberate the phenols, the dilute acetic acid acting also as a solvent for the water-insoluble phenols. At least a 50 per cent concentration of acetic acid is required to maintain homogeneity. The phenol solution is treated with a few drops of sulfuric acid and nitric acid, warmed on the steam bath to effect



complete reaction as indicated by maximum development of yellow color. Making the solution ammoniacal results in rearrangement of the nitroso phenol to form the highly colored quinonoid salt. The intensity of this color is proportional to the concentration of the phenol.

The character of the color produced is somewhat influenced by the type of phenol involved; phenol itself, for instance, produces a greenish yellow color, whereas *p*-*tert*-butyl phenol produces an orange-yellow color. Since no other variations of the yellow color are encountered, either of the above two phenols may serve as standards in the colorimetric comparisons. Clear solutions are invariably obtained and direct comparison with standard phenol solutions may be made either in a Duboscq or Klett colorimeter or by the use of Nessler tubes; check results on separate extractions may be obtained within 5 to 10 parts per million. The method is rapid and direct, requiring no special apparatus other than that found in the average chemical laboratory.

### Experimental Details

**APPARATUS AND REAGENTS.** A Duboscq or a Klett colorimeter provided with 100-mm. tubes. Dilute potassium hydroxide solution, approximately 0.2 *N* in aqueous solution. Dilute sulfuric acid solution, approximately 0.2 *N* in aqueous solution. These solutions need not be standardized.

**Stock phenol solution.** Exactly 2 grams, accurately weighed, of freshly distilled or crystalline phenol are dissolved in 1 liter of distilled water. From this stock solution, which contains 2000 p. p. m., standard solutions of the desired concentrations are prepared. Diluted to 1 liter:

25 ml. of stock solution =	50 p. p. m. of standard
50 ml. of stock solution =	100 p. p. m. of standard
100 ml. of stock solution =	200 p. p. m. of standard

Standard solutions containing more than 200 p. p. m. should not be used because of the intense color produced in the nitrosation reaction. The color produced from these standards is a greenish yellow.

**Stock *p*-*tert*-butyl phenol solution.** Exactly 1 gram, accurately weighed, of *p*-*tert*-butyl phenol (Eastman Kodak Co. organic chemical P-2465) is dissolved in 250 ml. of glacial acetic acid and the solution is diluted to 500 ml. with distilled water. Standard solutions are prepared from this solution exactly as described above for the phenol solutions. This standard produces an orange-yellow color and is the one more often used in the actual comparisons. The dilutions should not be made until they are required, since the phenol has a tendency to precipitate.

**PROCEDURE.** A 25-ml. sample of the hydrocarbon solvent is placed in a 100-ml. Squibb separatory funnel and extracted several times with 25-ml. portions of 0.2 *N* potassium hydroxide until additional extractions yield no color when treated as directed below. From one to five extractions are usually sufficient.

Each 25-ml. extract is separated into a 100-ml. volumetric flask, and neutralized by adding 25 ml. of 0.2 *N* sulfuric acid from a graduate. It is diluted to the mark with glacial acetic acid and mixed by shaking. Fifty milliliters of this solution are placed in a 125-ml. Erlenmeyer flask and 6 drops of concentrated sulfuric acid and 6 drops of nitric acid are added. It is heated on the steam bath until a pale yellow color develops and reaches a maximum, requiring from 5 to 30 minutes. The remaining 50-ml. aliquot of the original solution should be treated in a like manner as a check.

After cooling in ice, the pale yellow solution is cautiously made alkaline by the gradual addition of at least 35 ml. of concentrated ammonium hydroxide (sp. gr. 0.90), resulting in a considerable increase in color intensity. A greater excess of ammonium hydroxide does no harm. After dilution to 100 ml. with distilled water, the solution is compared in a colorimeter with a suitable standard, as described below. The calculated phenol contents of each of the several extractions are added to give the total phenol content of the solvent, expressed as parts per million of the particular phenol used as a standard.

As a check on the above procedure, another 25-ml. sample of the solvent is extracted with as many 25-ml. portions of 0.2 *N* potassium hydroxide as were found necessary in the previous determination. The total extracts are combined and a 25-ml. aliquot is placed in a 100-ml. volumetric flask, neutralized with 0.2 *N* sulfuric acid, and adjusted to a 100-ml. final volume by addition of glacial acetic acid. After thorough mixing, two 50-ml. aliquot portions are warmed with the mixed acids, then

made ammoniacal and otherwise treated as above. The calculated phenol content of this aliquot is multiplied by the total number of 25-ml. alkali extractions that were required to remove all phenols from the solvent; this value gives the total phenol content of the solvent and should check within 2 to 5 per cent of the previous value which was obtained by the summation of the phenol contents of the individual extractions.

**PREPARATION OF THE STANDARDS.** Various shades of yellow are obtained, depending on the type of phenol present in the sample of solvent. This fact makes it necessary to employ different phenols as standards for comparison. In practice, only two tints have actually been obtained. Phenol may be used if the unknown shows a greenish yellow color on treatment; *p*-*tert*-butyl phenol yields by a similar treatment an orange-yellow color. No difficulty is experienced in deciding which is the proper phenol to use in preparing the standards for the colorimetric comparison.

It is necessary to compare the unknown with a standard having approximately the same phenol concentration—that is, within 50 p. p. m. For this reason, three standards must be prepared containing 50, 100, and 200 p. p. m., respectively. Twenty-five milliliters of each standard (containing 50, 100, and 200 p. p. m., respectively) are then treated exactly as described for the unknown. The selection of the proper standard for the comparison may be readily decided by comparison with the unknown. If the first extraction of the solvent produces a color intensity corresponding to a phenol content greater than 250 to 300 p. p. m., it should be diluted with distilled water to a convenient phenol content within the range of the standards.

The colors produced are stable, the useful life of the standards being about 2 weeks, during which time they remain practically constant. After a month's standing, however, the apparent phenol content of the standards, as indicated by the color change, has decreased from 5 to 15 per cent. It is recommended that fresh standards be prepared at the time that the colorimetric comparison is to be made.

### Discussion of Analytical Method

Repeated alkaline treatment of the solvent is required in order to ensure complete extraction of the phenols. Solvents containing 300 to 600 p. p. m. require at least five successive extractions; lower concentrations require only four. If the phenol content is only 10 to 20 p. p. m., one extraction suffices. This protracted extraction method has been found necessary because of the low solubility of the alkali salts of the phenols involved. Since the phenols are already in a free state in the solvents, no preliminary saponification treatment need be given.

It is unnecessary to know the identity of the phenols being estimated, since the method described is primarily for specification control or similar purposes. The fact that *p*-*tert*-butyl phenol is usually the required standard indicates that we are dealing with mixtures of alkylated phenols which have boiling points within or only slightly higher than the boiling range of the petroleum solvents in question. Stoughton (3) has indicated that hydrocarbons such as toluene might interfere. However, the authors have never encountered such interference by any of the petroleum solvents with which they have worked, most of which are highly aromatic in character. Continued alkaline treatment eventually produces an extract which yields no color whatsoever on acid treatment.

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# Determination of the Molecular Weights of Oils

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An apparatus consisting essentially of a modified form of the Cottrell boiler and adapted for use with the Menzies-Wright water differential thermometer is described. Benzene or cyclohexane may be used as solvent. Benzene is to be preferred, since a good grade of commercial product requires no further purification and may be used directly. Results on pure compounds and a variety of hydrocarbon materials indicate a precision of 1 per cent or better at all times. A complete molecular weight determination requires about 2 hours; however, with the necessary equipment, two or three determinations may be carried out simultaneously.

RECENT work on the constitution of petroleum, and, in particular, the chemical structure of closely cut petroleum distillates, has shown that some rather striking relationships exist among the physico-chemical properties of an oil and the proportion of the various types of hydrocarbon molecules present. The molecular weight of an oil is important, not only for its own interest, but also because of its appearance with density, viscosity, refractive index, surface tension, etc., in a number of functions which have been developed for purposes of correlating and characterizing these materials.

Unfortunately, the molecular weight of an oil is not easy to determine. The best methods available at present involve the determination of the effective molecular weight, in some particular solvent, at several concentrations, by either a cryoscopic or an ebullioscopic method and an extrapolation of the data to zero concentration of solute. Theoretically, this value should be the weighted harmonic mean of all the constituents present.

Rall and Smith (5) of the Bureau of Mines recently conducted a survey of the cryoscopic methods in use in a number of laboratories in which research on petroleum products was being carried out. The individual results on four oils examined by each laboratory were not particularly concordant. They were analyzed and compared with the results obtained by the bureau's apparatus, with the conclusion that the only safe procedure is to use the purest solvent possible and to determine the cryoscopic constant with a known pure solute. The low solubility at the freezing point of the solvent and the tendency on the part of some solutes to form mixed crystals with the solvent introduce inherent errors in this method.

Mair (2) at the Bureau of Standards has investigated the ebullioscopic method for the molecular weights of oil fractions and has developed an apparatus capable of giving results on pure compounds which are within 1 per cent of the theoretical value. While this method obviates many of the difficulties inherent in the cryoscopic procedure, it is limited to oils having a negligible vapor pressure at the boiling temperature of the solvent. Fortunately, most waxes and lubricating oils fall in this class.

As in the case of the apparatus used by Rall and Smith, the equipment described by Mair is applicable only in research projects, its complexity making it unsuitable for routine

laboratory use. The present paper describes the construction and use of a simple ebullioscopic apparatus for the routine determination of the molecular weights of involatile oils. It was developed in this laboratory as the result of a need which arose in connection with work on the chemical constitution of oils.

## Apparatus

The apparatus is essentially a modified form of the Cottrell (1) boiler adapted for use with the Menzies-Wright (3, 4) water differential thermometer. A diagram of the equipment is given in Figure 1.

The boiler is designed to hold from 25 to 30 cc. of solvent, bringing the normal liquid level to the point at which the tube begins to widen. The additions of solute during the course of a run, therefore, cause no substantial rise in the liquid level and, hence, negligible change in the pumping conditions. Surrounding the boiler is a jacket, and the annular space is under high vacuum. The use of a vacuum jacket minimizes the heat loss from the apparatus and protects the boiler from laboratory drafts.

Heat is supplied electrically through a chromel coil placed directly in contact with the liquid. The coil, formed from No. 24 wire, has a resistance of 0.9 ohm. The optimum power consumption is about 30 watts. This wire is brazed onto two tungsten leads which are brought through the vacuum jacket and into the boiler by the use of GT 70 tungsten sealing glass presses. In use, it has been found convenient to make connections with the tungsten leads by means of a small Bakelite block containing two mercury wells (Figure 1).

The vapor-lift pump is attached rigidly to the boiler at the top and bottom and thus serves to hold the water thermometer in place. The tube leading from the large bell to the inverted cup is of only 2-mm. diameter and has a relatively thin wall.

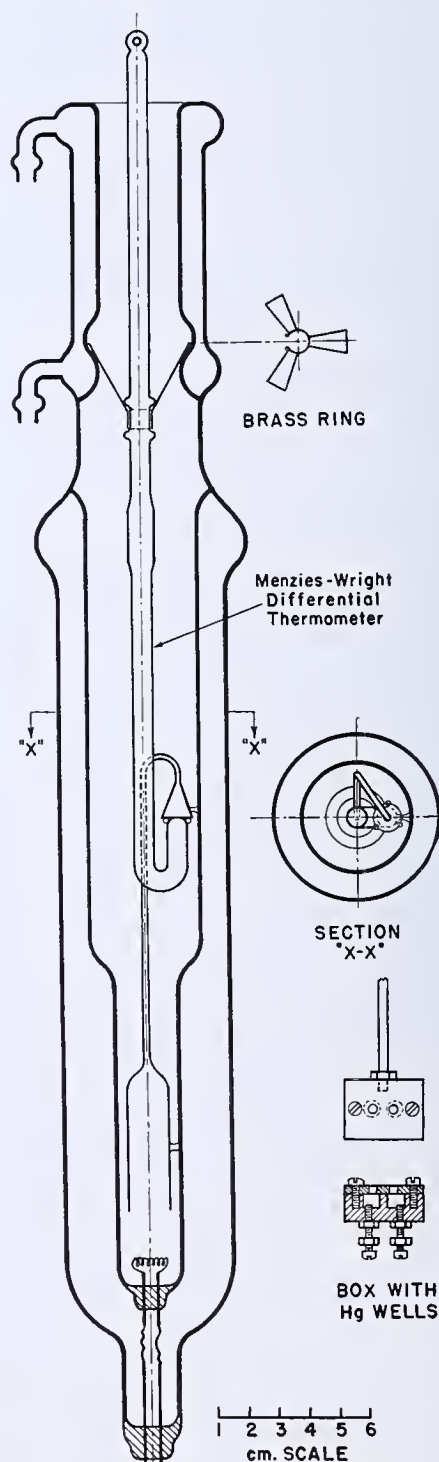


FIGURE 1. DIAGRAM



TABLE I. MOLECULAR WEIGHT DETERMINATIONS

Material	Calculated	In Benzene	In Cyclohexane	Freezing Point, Benzene
Triphenyl methane, Eastman Kodak, m. p. 93-94° C.	244.1	$K = 54.4 \pm 0.1$	$K = 61.8 \pm 0.2$	...
Anthracene, sublimed and recrystallized twice from benzene	178.1	$178.0 \pm 1.0$	$179.6 \pm 0.7$	...
Benzil, Eastman Kodak, m. p. 94-95° C.	210.1	$211.6 \pm 1.3$	$210.6 \pm 1.1$	...
U. S. Bureau of Mines oil:				
No. 1	...	$671 \pm 5$	$652 \pm 3^a$	764
No. 2	...	$450 \pm 1$	$445 \pm 2^a$	442
No. 3	...	$326 \pm 2$	$312 \pm 2$	358
No. 4	...	$208 \pm 1$	$208.5 \pm 2$	218
Refined mid-continent residuum	...	$1010 \pm 8^a$	$908 \pm 5^a$	900
Paraffinic molecular still residuum	...	$1553 \pm 7^a$	$1459 \pm 10^a$	...
Heavy naphthenic distillate	...	$522 \pm 2^a$	$465 \pm 2$	511
Paraffin, m. p. 132° F.	...	$380 \pm 1$	$352 \pm 2$	...
Synthetic paraffin wax, m. p. 98° C.	...	$750 \pm 5$	$762 \pm 4^a$	...

<sup>a</sup> Negative molecular weight concentration slope.

The condenser at the top of the boiler has been made fairly wide to admit the thermometer and to allow for easy addition of solute. A slight bulb is blown in the lower inner wall to act as support for the thermometer collar, illustrated in Figure 1, which is formed from 0.25-mm. (0.010-inch) brass shim stock. The three vanes rest in the depression in the condenser wall, and by adjusting the angle which they make with the stem, any degree of upward thrust can be given the thermometer. An important function of the brass collar is its action as a condenser. The vanes lying against the cold condenser wall are cooled and, during a run, an appreciable amount of solvent condenses on the brass ring and is reheated to the boiling point on the upper bulb of the thermometer. In practice, after the power input exceeds a certain critical value, rapid refluxing takes place at the base of the condenser but no vapors ever rise in the condenser. This assures, in addition to a constant vapor volume, a negligible loss of solvent. These observations were made with reference to benzene and cyclohexane as solvents.

For a successful determination, it is essential that the boiling be smooth. When functioning properly, the vapor passing up through the vapor-lift pump carries with it a heavy film of solution along the wall. The appearance of any slugs of liquid always makes for unsteady temperatures. Solution drips from the bottom bulb at the rate of 2 to 3 drops per second. After the first addition of solute is made, there is seldom any difficulty with the boiling. The type of boiling obtained with pure solvent, however, is less desirable and to get the zero point for the thermometer it may be necessary to average several readings. Once this zero point is obtained, it may be used for any determination, since its value is a function only of the dimensions of the thermometer itself and the purity and boiling point of the solvent. It has been found possible to get the zero point more quickly by dispersing a small amount of gum rubber (about 0.05 per cent) in the solvent. Good boiling results without any measurable rise in the boiling point. This rubber solution may also be used as solvent in the few cases in which poor pumping action persists after the addition of solute. The reading of the meniscus in the small bulb of the thermometer may also be dispensed with as soon as the relation between the heights of liquid in the two arms has been established. For a well-constructed thermometer, the relationship is, of course, strictly linear.

### Experimental Results

A solvent chosen for the routine examination of oils should be obtainable in quantity and in a moderate degree of purity. In addition, a convenient boiling point and a large ebullioscopic constant are desirable. Adequate solvent properties for hydrocarbons and stability under the operating conditions are essential. (Owing to decomposition on the heated coil, it is not possible to use the common chlorinated solvents.) Benzene and cyclohexane are the only solvents which meet these requirements.

For this work, the cyclohexane was purified by treatment with concentrated sulfuric acid, followed by an alkali wash. This material was then fractionated in a 45-plate column still, retaining the middle third of the distillate for experimental use. The benzene used was a good grade of "nitration benzene"; no purification or drying was found necessary.

Results were obtained on a number of pure compounds, three of which are listed in Table I. In every case the precision was 1 per cent or better; the accuracy was also about 1 per cent. These three compounds were selected because they are substances which may be obtained in reasonable purity and used conveniently as calibrating compounds. The experimental values for anthracene and benzil are based on the ebullioscopic constant obtained

using triphenyl methane.

To illustrate the behavior with oils and waxes, the results of a number of determinations on materials of rather widely differing properties have been tabulated in Table I. The concordance in the experimental results is again seen to be better than 1 per cent. For purposes of comparison, the four oils used by Rall and Smith (1) in their survey were examined and are listed. These oils have been preserved in tightly sealed bottles and kept in the dark. In the extreme right-hand column are listed the values obtained in this laboratory by the cryoscopic method, using purified benzene as solvent. The estimated probable error in these determinations is 3 per cent.

Throughout the work there was observed no tendency on the part of any substance to increase in apparent molecular weight with concentration. With the exception of those runs noted in Table I, the molecular weight-concentration curves were, within the limits of error, lines parallel to the concentration axis. Thus, in calculating the experimental molecular weight, a simple average of the four or five readings was taken. The limits of error noted are the mean deviations from the averaged value. Apparently the tendency of substances in general to associate is very small at the temperatures of boiling benzene or boiling cyclohexane and in the concentration range studied (maximum concentration approximately 0.15 molar).

It is evident from the tabulated results on the petroleum products that, while the values are reproducible with a precision of 1 per cent or better, it is not possible to speak of the accuracy of the determination. Differences as great as 10 per cent may exist between the values for the molecular weights of an oil or wax in boiling benzene and cyclohexane, and even greater differences are observed when the values obtained by the freezing point method are compared with those using an ebullioscopic procedure. These differences are apparently more pronounced at high values of the molecular weight. By adhering to a single solvent, however, comparable results may be expected. In this laboratory a good quality "nitration benzene" or any "reagent" product is used exclusively. Owing to the fact that they require no further purification, these solvents are preferred to cyclohexane.

It is believed that this apparatus offers a convenient and reasonably precise means for the routine examination of petroleum products. The time required for a single determination is about 2 hours. Since it is necessary to allow from 10 to 15 minutes for equilibrium to be established after each addition of solute, it would be possible for an operator, with the necessary equipment, to carry out two or three determinations simultaneously.

The method described is the best with regard to both speed and accuracy of several investigated at this laboratory, in-



cluding the original one using the Menzies-Wright differential thermometer.

### Acknowledgment

The writers are indebted to William E. Barr, of the Gulf Research and Development Co., for his patient and skillful glass working.

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# Photoelectric Colorimetry

## An Optical Study of Permanganate Ion and of the Chromium-Diphenyl Carbazide System

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The colorimetric determination of manganese by the periodate method and the determination of chromium by diphenyl carbazide have been studied with the object of adapting them to photoelectric colorimetry. An optical method for the separation of interfering ions is discussed in connection with the manganese method.

RECENTLY, with the advent and adoption of photoelectric cells, numerous photoelectric colorimeters have been designed for chemical analysis. It now seems advisable to study several standard colorimetric methods, using a colorimeter which is constructed with due cognizance of true optical principles without the use of certain well-known refinements which none of these instruments employs (such as the use of a monochromatic source of illumination). The purpose here is to determine what precision may be expected in the use of such an instrument, what necessary changes must be made in existing methods to adapt them to photoelectric colorimetry, and the effect of certain optical properties of these systems on their use as general analytical methods.

That the fundamental law of light absorption, the Lambert-Beer relationship, should form the basis for every exact colorimetric method has been shown by Müller (6). In this investigation the conformity of the absorbing entity to this relationship was used as the criterion of an acceptable method. Only those solutions that yielded absorption values within the range of conformity were used; others were diluted until they fell within that range. This working range is that in which the extinction coefficient is invariant, within the limits of experimental error.

### Apparatus

Two photoelectric colorimeters were used in this work, both of which have been described previously (6, 7). Preliminary measurements were made using the photronic cell instrument, by the use of which a photometric precision of 0.5 to 1 per cent is obtained. Final measurements were made using a colorimeter employing a vacuum photocell and triode (7), used in a slide-back type of vacuum-tube voltmeter. The compensating potential in the grid circuit is supplied by a dial and slide-wire potentiometer which can be calibrated to read transmission values directly. A photometric precision of 0.03 to 0.05 per cent can be realized by using this instrument.

Both colorimeters were subjected to physical calibration by means of nonselective wire screens of known transmission. With this assurance of linear response, conformity with Beer's law for

any system is unlikely to be the result of mutually compensating errors.

Absorption spectra of the various colored compounds and the transmission spectra of the light filters were measured with a Bausch & Lomb spectrophotometer which was calibrated periodically with a mercury arc.

### Determination of Manganese

The oxidation of manganous ion to permanganate by periodate in acid solution as described by Willard and Great-house (9) is free from many of the disturbing factors arising from the use of other oxidizing agents. The reaction is given by the equation

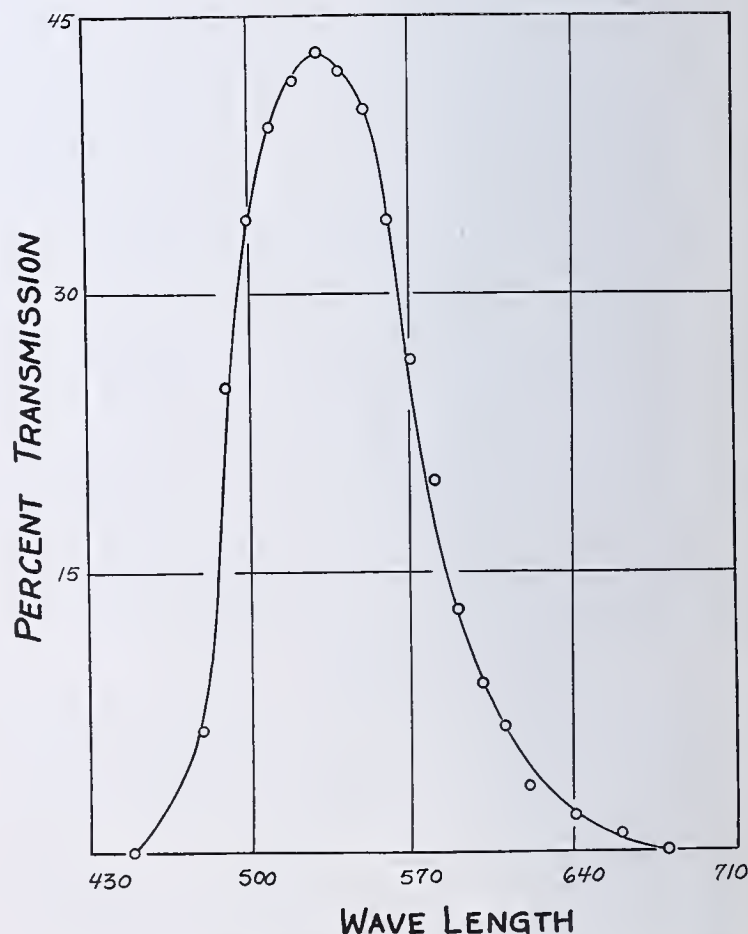
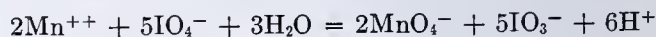


FIGURE 1. TRANSMISSION SPECTRUM OF SEXTANT GREEN FILTER



Wide application has been made of this method and it has been employed satisfactorily for a long time; therefore it seemed well adapted to the photoelectric technique.

From a consideration of the absorption spectrum of permanganate ion which has been determined by Lange and Schusterius (5), the desired region of wave lengths to be used in the determination of permanganate can be found. (The region of maximum absorption should be used in making the measurement.) The presence of a prominent absorption band at  $526\text{ m}\mu$  indicates that a highly selective green light filter must be used for the measurements. A Corning sextant green filter 2 mm. thick was used to isolate this band. The transmission spectrum of this filter is shown in Figure 1. Owing to the marked change in absorption of permanganate even in this narrow ( $80\text{-m}\mu$ ) spectral region, the validity of Beer's law must be tested using various concentrations of permanganate to ascertain the working limits for photometry.

Figure 2 shows the close agreement with Beer's law up to a concentration of 8.4 mg. of manganese per liter. The ordinates represent the extinction ( $\log I_0/I$ ), while the abscissas are measured in milligrams of manganese per liter. From this curve the milligram extinction coefficient was calculated and this value was then used in calculating the results of the photometric measurements. If the photonic cell instrument is used, the linear behavior may be extended to 12 mg. of manganese per liter, at the expense of precision. The extension of the range is due only to the high green sensitivity of the barrier-type photocells.

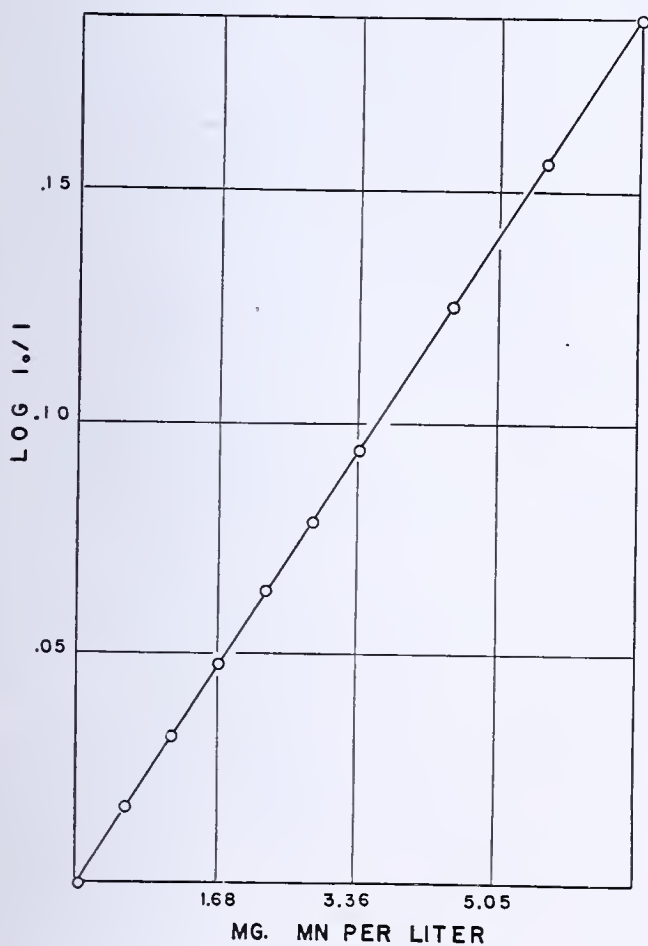


FIGURE 2

In conditioning the solution preparative to photometering it, the method of Willard and Greathouse (9) was followed. In all cases the photometric measurements were made using standard substitution technique in which a cup containing distilled water first intercepts the light beam giving the  $I_0$  reading. The permanganate solution in a matched cup is

then substituted (giving the  $I$  reading), and finally the  $I_0$  reading is checked.

**INTERFERENCE DUE TO OTHER COLORED IONS.** In many applications of this method the manganese will be accompanied by other metals which yield colored ions upon solution of the sample and subsequent oxidation with periodate. It has been customary in colorimetry to compensate for this extraneous light absorption by making some sort of arbitrary adjustment—by adding coloring materials to the standard solution, or by interposing in the light beam from the standard cup a light filter which simulates the effect of the background color. Not only do these methods depend largely upon the judgment of the analyst, but they are at best crude attempts to approximate unknown conditions and concentrations.

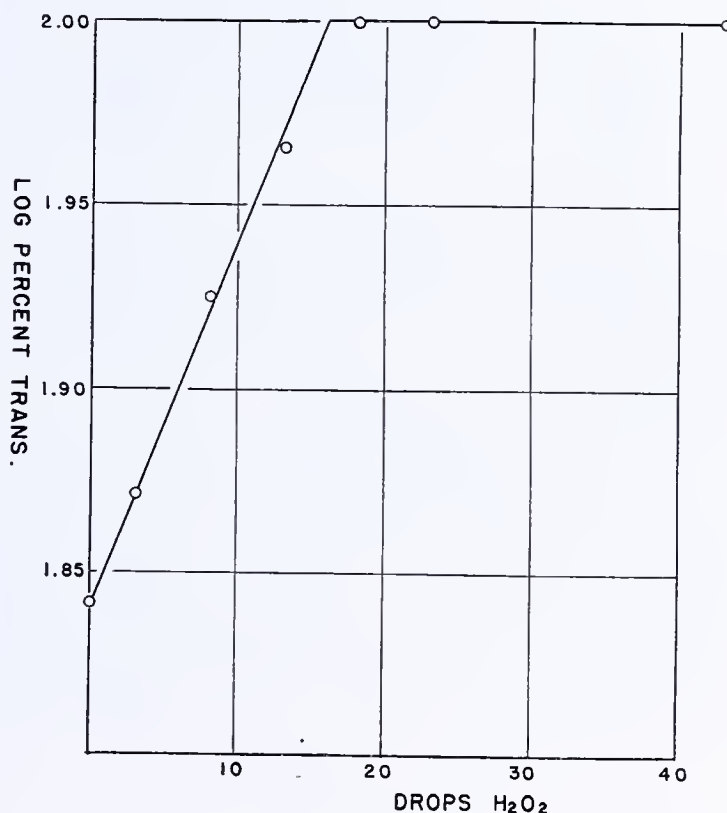


FIGURE 3. PHOTOELECTRIC TITRATION OF PERMANGANATE WITH HYDROGEN PEROXIDE

In order to circumvent this difficulty without resorting to chemical separations of the interfering ions, it was attempted to bleach a portion of the test solution and, after freeing it from permanganate, use it for obtaining the  $I_0$  value. It was found that the addition of a few drops of very dilute hydrogen peroxide (approximately 0.01 per cent) to a portion of the oxidized solution would remove the permanganate and leave the background color.

Certain objections to this method would seem to arise: (1) reaction of excess hydrogen peroxide with periodate; (2) the formation of peroxides of other components that would in themselves color the solution; and (3) reoxidation of manganese by excess periodate (which is always present).

The first objection was met by performing a photoelectric titration of a solution containing sulfuric acid, permanganate, and periodate with dilute hydrogen peroxide. Figure 3 shows that no further color is obtained by adding to such a solution excess hydrogen peroxide after the permanganate is reduced. A fivefold excess of hydrogen peroxide (not shown in plot) over the amount necessary to reduce the permanganate gave no indication of color.

An evaluation of the magnitude of the error introduced when colored metal peroxides are present may be gained by a comparison of their molar extinction coefficients with that of



the permanganate ion. These extinction coefficients were determined at 520 m $\mu$  since the sextant green filter possesses its maximum transmission at that wave length. The values obtained are shown in Table I along with the tolerance ratio that will permit the determination of manganese to  $\pm 1$  per cent precision. However, these figures represent maximum error, since an excess of hydrogen peroxide must be added in order to develop the full color in these peroxides, while in actual work hydrogen peroxide is added only until the permanganate color is discharged.

Studies on the rate of oxidation of manganous ion to permanganate ion showed that the third objection was of no consequence, since the rate of reoxidation at room temperature is immeasurably slow.

TABLE I. EXTINCTION COEFFICIENTS

Colored Compound	Molar Extinction Coefficient, 520 m $\mu$	Tolerance Ratio
TiO <sub>3</sub>	98.1	0.397
HVO <sub>4</sub>	269	0.077
H <sub>2</sub> MoO <sub>5</sub>	0.973	19.62
HMnO <sub>4</sub>	2230	...

In a critical study of this method involving the use of a bleached aliquot as a blank, the question arises: Does the accuracy of the photometric method warrant the use of the "bleached blank" and does a real difference exist between values obtained in this way and those obtained using water in the comparison cup?

An evaluation of this difference can be made by analyzing a standard sample using both types of comparison blanks. This has been done and some representative results of the analysis of a standard steel using both water and reduced aliquot blanks are shown in Table II. The samples were dissolved in a nitric-sulfuric acid mixture, and phosphoric acid was added to decolorize the iron. Solid sodium periodate was added and the solution was boiled for 2 minutes. It was then cooled to 20° C. and diluted to an appropriate volume in a volumetric flask. This solution was used in making the photometric measurements.

TABLE II. ANALYSIS OF STEEL

(Sample analyzed, U. S. Bureau of Standards Steel No. 106, Certificate Value 0.481% Mn)

Sample	Manganese Found	
	H <sub>2</sub> O blank %	Reduced blank %
1	0.515	0.483
2	0.506	0.482
3	0.507	0.483
4	0.529	0.485

The results obtained from using the water blank in addition to being approximately 6 per cent high (on the average) are erratic. For this reason the popular, but always questionable, procedure of "using a factor" is doubly dangerous in this case. The reduced blank values not only agree well between themselves but also with the certified value of the sample.

TABLE III. RESULTS WITH SODIUM AZIDE

Interfering Ion Mg./l.	Mn Present Mg./l.	Mn Found Mg./l.
300 Mo	3.00	3.00
600 Ti	6.00	6.12
800 V	8.00	7.80
500 Cr	5.00	4.94

ALTERNATIVE BLEACHING PROCEDURE. In the event that interfering metals are present in amounts such that the tolerance ratios are approached or exceeded, sodium azide can be used in lieu of hydrogen peroxide as the reducing agent. In this procedure a few milligrams of the solid sodium azide are added to the solution to be prepared for use as a blank.

The reduction is somewhat slower than in the case of the peroxide. The use of sodium azide, however, to produce a comparison blank gave results accurate to about 1 to 2 per cent, on the average, when used in solutions containing a hundredfold excess of interfering ion. Some typical results obtained by using this method are shown in Table III.

Chromium-Diphenyl Carbazide System

Cazeneuve (2) first suggested the use of diphenyl carbazide as a colorimetric reagent for chromium as a result of his study of the various colored metal compounds that diphenyl carbazide forms. The optics of this reaction were studied for a twofold reason. First, it is an example of the adaption of the technique of photoelectric photometry to an organic color-producing reagent; and secondly, the sensitivity of the method, or more strictly the high extinction coefficient of the chromium compound, indicates that the method is of microchemical significance. The analysis of microgram quantities of chromium by this method is therefore practical.

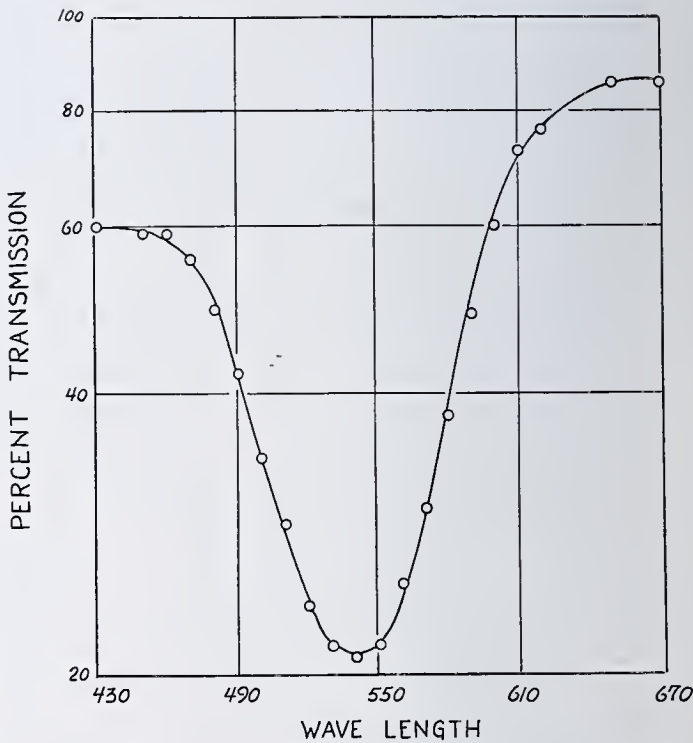


FIGURE 4. ABSORPTION SPECTRUM OF CHROMIUM-DIPHENYL CARBAZIDE COMPLEX

This color reaction has had wide application since its discovery. It has been used as an indicator in dichromate oxidimetry (1), as a qualitative reagent for chromium (4, 8), and as a reagent for chromium in a spectrographic analysis of tissue (3) based on the absorption spectrum of the colored compound.

When trial solutions were prepared using an acetic acid-alcohol solution of diphenyl carbazide as suggested by Cazeneuve (2), the color of the solution was slow in developing, full color being developed only after 20 minutes. A more serious disadvantage also was noted, in that the color so formed showed a tendency to fade. Qualitative experiments bore out Stover's conclusion that the presence of acetic acid was the disturbing factor. Further experiments indicated that acidification with sulfuric acid increased the color stability and brought about instantaneous development of full color. Furthermore, it was found that solutions acidified in this manner and containing mercury, copper, and ferric iron (the interfering metals mentioned by Cazeneuve) developed no color. For these reasons a saturated solution of diphenyl carbazide in 95 per cent ethyl alcohol was used as the color



reagent in the following experiments, and for each 100 cc. of dichromate solution (made approximately 0.1 molar with sulfuric acid) 1 cc. of this reagent was used. That the color stability is sufficient for accurate analysis under these conditions is shown in Table IV, the data covering the concentration range where Beer's law is valid for this system under the optical conditions indicated.

TABLE IV. USE OF DIPHENYL CARBAZIDE

Chromium Micrograms/l.	$I/I_0$ on Addition of Reagent	$I/I_0$ after 0.5 Hour	$I/I_0$ after 15 Hours
125	83.1	82.7	84.4
250	69.8	70.2	72.2
375	59.8	60.1	63.0
500	50.2	50.3	54.9
625	42.8	42.8	46.2

In order to determine the proper filter to use for photometry, the absorption spectrum of the chromium-diphenyl carbazide complex was determined using a  $2.06 \times 10^{-6}$  molar potassium dichromate solution which had been treated before final dilution in the manner previously described to develop the color. The compound was found to have a fairly broad absorption band in the green (Figure 4) as found by Dingwall, Croesen, and Beans (3). The molar extinction coefficient calculated on the basis of the molarity of the dichromate solution resulted in a value of  $8.14 \times 10^4$  at 540  $m\mu$ . From these data it is seen that the sextant green filter used in the permanganate studies should also be used in this case. Using this filter with the vacuum photocell vacuum-tube voltmeter colorimeter, the diphenyl carbazide-chromium system was found to conform to Beer's law in all concentra-

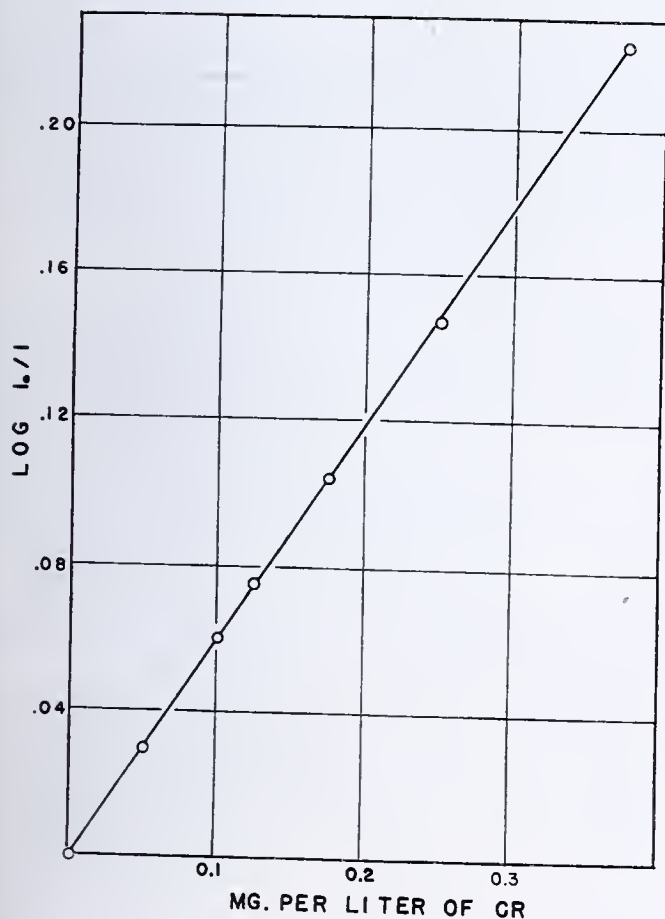


FIGURE 5

tions below  $3.6 \times 10^{-4}$  molar dichromate. This corresponds to a concentration of 375 micrograms of chromium per liter. The conformity of this system to Beer's law is shown graphically in Figure 5.

**INTERFERENCE OF OTHER METALS.** If for any reason the use of sulfuric acid is inadvisable and the sample to be ana-

lyzed is known to contain a high percentage of iron, is it possible to neglect the iron color under the conditions of photometry used in these experiments? Other investigators (3) measured the absorption spectrum of the iron compound and found that its maximum occurred at about 380  $m\mu$ . From the transmission value read from their curve of the absorption spectrum (for a solution containing 100 mg. of ferric iron per liter, measured through a 2-cm. depth) the molar extinction coefficient at 460  $m\mu$  was calculated to be 5. The approximate cutoff of the sextant green filter is 460  $m\mu$ . At 500  $m\mu$  the solution transmits 100 per cent of the incident light. Hence, interference due to iron may be neglected entirely when this green filter is used.

In addition to the interfering metals noted by Cazeneuve, molybdenum when present as molybdate in 0.1 molar sulfuric acid solution yields a violet colloidal suspension, its extinction coefficient being roughly  $5 \times 10^2$ . Therefore with any ratio of molybdenum to chromium less than 10, results with an accuracy of 1 per cent may be obtained by neglecting any color due to molybdenum.

### Summary

The periodate method of Willard and Greathouse for the colorimetric determination of manganese has been studied for the purpose of adapting it for use with a photoelectric colorimeter. Since the most convenient method of making the measurements is that of substitution photometry, a study of the optical properties of permanganate solutions with and without interfering ions has been made.

Two chemical methods of effecting optical separation of interfering ions have been developed in which the permanganate color is removed in an aliquot of the sample solution and this solution used to furnish the  $I_0$  (100 per cent transmission) value.

Data of a confirmatory nature regarding the use of these optical separatory methods are shown.

An optical study of the diphenyl carbazide-dichromate system has been made.

### Acknowledgment

The author is greatly indebted to Ralph H. Müller who suggested this work and under whose able direction it was carried out.

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TAKEN from a thesis submitted by George P. Rowland, Jr., in partial fulfillment of the requirements for the degree of doctor of philosophy at New York University.

### Correction

In the article on "Determination of Tetraethyllead in Gasoline" [*IND. ENG. CHEM., Anal. Ed.*, **11**, 324 (1939)] there is an error in the second sentence of the fifth paragraph under "Procedure." This sentence should read:

"To the dry lead chloride add 3 ml. of nitric acid."

CHARLES M. GAMBRILL



# Determination of Total Sulfur in Asphalts

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YOUNG (22) recently applied the method of Brunck (6) to the determination of organic sulfur and stated that accuracy was obtainable even by the employment of relatively simple apparatus.

In 1923 the author became interested in the determination of sulfur in asphalt and other bitumens in connection with a study of the reaction of sulfur with free magnesia present in asbestos used in the manufacture of bituminous cold-molded compositions. As the bomb equipment was not available, it became necessary to seek and develop a simple and accurate method for determining sulfur in bitumens by utilizing inexpensive and readily available apparatus. Accordingly, a thorough search of the literature relating to the determination of sulfur in organic substances was made.

## Methods Investigated

The methods of Falcicola (8), David and Fourcar (7), and Losana (17), as well as the alumino-thermite procedure (2, 3) and a method depending on the oxidation of sulfur vapor from the volatilized asphalt by passing with air through highly heated alundum (13), were thoroughly investigated; for various reasons it was found necessary to discard all of these. A method of combustion developed by Brunck (5) and Maderna (18) proved to be the most promising.

## Development of Method

A detailed study of the catalytic method discussed by Brunck, involving the preparation of nickel sesquioxide and cobalt sesquioxide by various procedures, including activation, was made. Combustion behavior was also carefully investigated.

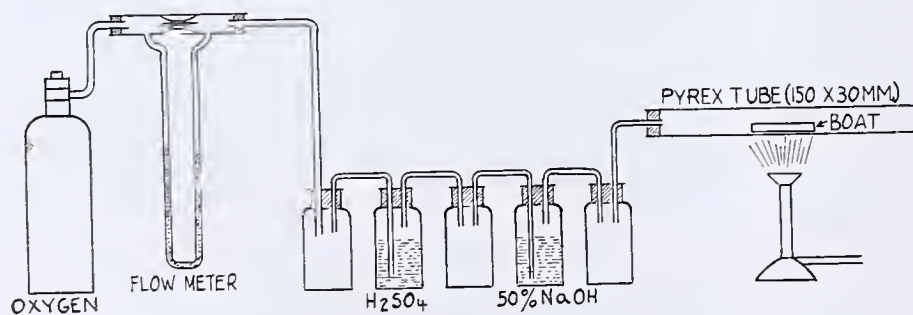


DIAGRAM OF APPARATUS

It was observed, however, that sulfides persistently formed with these oxides—probably nickel sulfide, cobalt sulfide, and some sodium sulfide. Because of the insolubility of nickel and cobalt sulfides, a loss resulted. Activation by the presence of a rare metal was ineffective. It was found impossible to oxidize these sulfides by digesting with water containing the common oxidizing agents (such as bromine and hydrogen peroxide). Commercial oxides, as purchased, proved unsatisfactory and were discarded.

In view of the strong oxidizing activity of a mixture of 60 parts of manganese dioxide and 40 parts of cupric oxide, which has been described in the literature (1, 4, 9-11, 15, 16, 19-21), its possible use as a catalyst in this case was investigated. Numerous trials were made with this catalyst and in none of the large number of determinations was the formation of sulfides detected. Also, the results agree closely with the sulfur content as determined by the bomb method. This is clearly evident from an examination of Table I.

TABLE I. DETERMINATION OF SULFUR IN ASPHALTS

	Sample 2173-24-A	Sample 2173-24-B	Sample 2173-24-C
S by bomb method, %	5.62, 5.80	3.27, 3.50	0.93, 1.01
S by method described, %	5.92, 5.75	3.48, 3.53	1.01, 1.01
	5.87, 5.94	3.53, 3.48	0.98, 0.98
	5.83, 5.84	....	....
	5.58, 5.67	....	....
	5.90, 5.88	....	....
	5.78, 5.90	....	....
	5.86, 5.96	....	....

## Method of Determining Total Sulfur in Asphalts

Based on the results of the investigation as outlined above, the following procedure was finally devised.

**PREPARATION OF THE CATALYST.** Manganese chloride tetrahydrate (411 grams) is dissolved in 500 ml. of water; to this is added a solution of 255 grams of cupric chloride dihydrate in 400 ml. of water. The solutions are thoroughly mixed, warmed, and stirred. A solution of 500 grams of potassium hydroxide in 500 ml. of water is then added drop by drop, stirred with uniformity, washed by decantation several times, filtered on a Büchner funnel, and washed free of alkali and chlorides. The mixed oxides are then dried in the steam bath overnight and finally at 200° to 225° C. until all the moisture has been driven off.

No advantage is gained by preparing this catalyst by precipitating cupric oxide from cupric nitrate trihydrate and sodium carbonate on manganese dioxide, prepared by the decomposition of potassium permanganate in concentrated nitric acid, according to Frémy (12). Frémy's oxide, while more active than the oxide prepared according to this method, causes the reaction to be so violent that loss through splattering is unavoidable. Commercial c. p. manganese dioxide also gave low results through splattering, as did Eschka's mixture when substituted for the sodium carbonate. Two parts of manganese dioxide-cupric oxide catalyst are then ground in a ball mill with one part of anhydrous sodium carbonate.

**COMBUSTION.** About 0.25 gram of asphalt (divided into small pieces) is placed in a porcelain combustion boat (15 × 100 mm.) and enough chloroform (about 3 ml.) is added to dissolve the sample. Enough of the catalytic combustion mixture is added to incorporate thoroughly with and cover the asphalt solution; this will usually require from 3 to 5 grams. The chloroform is then allowed to evaporate, preferably by setting the boat on a steam bath. The combustion boat is inserted in an open Pyrex glass tube (150 × 30 mm. with 2-mm. wall), one end of which is fitted with a stopper carrying a tube leading to an oxygen generator. More than one boat may be used in a tube, provided it is sufficiently long and combustions are carried on concurrently.

The oxygen is preferably passed through a train comprising a 50 per cent sodium hydroxide solution, followed by a wash bottle containing concentrated sulfuric acid. Empty bottles are placed between these for safety; a Venturi meter may be included to measure the flow of oxygen, but this is not essential. The Pyrex tube is supported horizontally on a semicylindrical and close-fitting metal shield lined with three thicknesses of asbestos paper, total about 0.3 cm. (0.125 inch) thick. It was found that by using the asbestos lined shield just enough heat was conducted for a smooth quiet combustion. The heat is insufficient to cause fusion between the glass and porcelain; thus the life of the Pyrex tube is greatly prolonged.

The oxygen is passed through the tube in a fairly rapid stream, about 10 ml. per second, and the tube is heated, at the zone where the boat is located, with a fishtail burner with a low flame at the start. When the combustion starts, as evidenced by the glowing of the asphalt-catalyst mixture, the flame is removed until the glowing ceases. To ensure complete oxidation, the tube is again heated for about one minute over a full flame. The oxy-



gen is then shut off and the tube and boat are allowed to cool. When cool, the boat and contents are digested with boiling water, filtered through double ordinary filter paper, and washed with boiling water (containing 1 to 2 per cent of sodium carbonate in order to prevent turbid washings due to carrying through of colloidal matter, 14). The filtrate is then made acid to Congo red with hydrochloric acid and refiltered on quantitative filter paper. A double filtration is desirable in order to free the filtrate completely from any colloidal matter that may have been carried through in the first filtration; quantitative paper is desirable. On the basis of a study of 26 determinations of the residue left on the filter in the second filtration, an average result of 0.0017 gram was obtained, which is too large to be neglected. The sulfates are precipitated in the filtrate with barium chloride according to standard practice. Blank determinations for sulfur content of the catalytic combustion mixture should be made and corrections applied.

### Conclusion

This modification of Brunck's method for sulfur determination, as applied to bitumens and asphalts, gives results concordant with the bomb method, and uses simple and readily available equipment. This modified method has been found entirely satisfactory.

### Acknowledgment

This work was performed during the years 1923 to 1927 in the laboratory of the Garfield Manufacturing Company, Garfield, N. J. Acknowledgment is gladly made to all who assisted in this work, and particularly to L. S. Miller of the Barber Asphalt Company, who furnished the asphalts.

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## Refractometric Determination of Soluble Solids in Citrus Juices

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THE standard method used in the citrus industry for estimating the total soluble solids content of citrus juices employs the Brix hydrometer. This is the legal method for testing maturity, by determining the ratio of total soluble solids to acid.

During the early development of the citrus by-products industry, the Brix spindle was generally employed in estimating the total soluble solids content of juice products, and the standards of composition of these products were based on this method. This was fairly satisfactory so long as simple products such as reamer-extracted juices were involved, but with the development of different types of natural-strength and concentrated juices and compounded products containing various added ingredients, difficulties were encountered and in some cases satisfactory results could not be obtained.

The refractometer offers an alternative method of determining soluble solids in citrus juice. In spite of a number of obvious advantages, this is also subject to certain errors and limitations and does not give the same results as the Brix spindle.

A number of factors are involved in the use of both methods. The Brix spindle method is based on changes in density of aqueous sucrose solutions with changes in the sucrose content. Actually, solutions of sugars other than sucrose have densities so near those of sucrose solutions that the Brix hydrometer may be considered accurate in them. Soluble materials other than sugars have variable and in most cases unknown effects on the Brix readings.

In the measurement of degrees Brix it is necessary, for best results, first to check the calibrations of the hydrometer, since many of those on the market are not accurately calibrated. The spindle should be thoroughly clean and dry. Measurements should be made in regulation hydrometer cylinders filled level with the ground-glass rim. The sample is preferably deaerated. In the case of finely screened, dilute juices this may not be necessary if the hydrometer is twirled to detach air bubbles as it is lowered into the liquid. A highly concentrated juice must be deaerated, and even then, if it is thick or viscous because of high soluble or insoluble solids or pectin, much time is required for the hydrometer to assume the equilibrium position. The sluggishness caused by excessive viscosity may result in serious error. Such difficulties may be partially eliminated by use of the dilution method, but this procedure has obvious objections in routine testing. Finally, the temperature should be close to the standard of 20° C., since the usual temperature corrections do not apply equally to sugar and nonsugar solids.

Similar precautions are necessary in the use of the refractometer. The prisms must be perfectly clean to be evenly wet by the solution under test and must be perfectly dry to prevent dilution of the test solution. Screening and deaeration of the sample improve the sharpness of the shadow and thereby enhance the precision and accuracy. For accurate results the readings should be made at 20° C. The errors introduced in applying temperature corrections are similar to those occurring with the Brix spindle.

The refractometer, used either with the sucrose scale or the regular refractive index scale and sugar table, and the Brix spindle should give identical results with pure sucrose solutions. Other solutes do not have the same effects as sucrose, however, and consequently when the two methods



are applied to complex solutions, such as citrus juices, different results are obtained.

In adapting the refractometer to various fruit juice products, several workers have recognized that its use is complicated by the diverse compositions of these products. Macara (2) recognized that errors are caused by citric acid, glucose solids, and invert sugar and gave data for applying corrections for these components. McRoberts (3) did a large amount of work on the determination of soluble solids in fruit products and showed that the refractometer is satisfactory for the purpose. He also obtained data by which corrections for citric or tartaric acid might be made.

The authors' work with citrus juices, involving analysis by the two methods of numerous samples of citrus juices and juice products and of prepared solutions of the different juice constituents, has indicated that the Brix spindle gives high values and that the refractometer gives low results. The constituents of citrus juices known to be important in this respect are citric acid, invert sugar, ash, insoluble solids, and essential oils. Since several factors are involved, the relation of the results obtained by the two methods is changed by natural variation in composition among different products. The greatest single variation is caused by citric acid and, consequently, the greatest difference between refractometer and Brix spindle values appears with highly acid products such as lemon juice, concentrated citrus juices, and certain types of beverage bases.

Because this error may amount to several per cent, it is necessary to apply some form of correction if the refractometer is to be used for routine analysis. There is some question as to whether this correction should be applied to give true soluble solids or degrees Brix, but since the use of the hydrometer method is well established, it appears desirable to correct to degrees Brix.

The over-all corrections to make refractometer sucrose scale values comparable with Brix values may be made in at least three ways: (1) by applying separate corrections for each of the above factors, determined on synthetic mixtures; (2) by applying empirical corrections determined for a large number of representative products with some constituent such as citric acid as an index of the magnitude of the correction; or (3) by applying a correction for citric acid only, this being the greatest single factor.

When these three methods and modifications of them were considered, it became obvious that none would be entirely

satisfactory because of the wide natural variation in composition of citrus juices. Method 1 would necessitate a fairly complete analysis of every sample before the correct solids could be ascertained and this would defeat the very purpose of the use of the refractometer. Methods 2 and 3 have been used experimentally, applying corrections based on data obtained on a large number of samples of orange, lemon, and grapefruit juices of different types and on synthetic solutions of sugar and citric acid. The corrections were used in both tabular and nomographic forms. This experience led the authors to adopt method 3 as tabulated herein for all routine work with citrus juice products, other than maturity testing.

### Procedure and Data

In obtaining data for correction tables a number of solutions of pure citric acid were prepared and the soluble solids, as sucrose, of the solutions were determined with the refractometer and the Brix spindle.

The citric acid was prepared by recrystallization of the ordinary U. S. P. grade of acid (from lemons). The acid was recrystallized four times from water by vacuum concentration in Pyrex glass apparatus at about 35° C. The final crystals, after being rinsed with cold water and drained as free of liquor as possible by suction, were dried to about 3.5 per cent moisture at about 40° C.

Solutions of different strengths, as shown in Table I, were prepared from this recrystallized acid with boiled, carbon dioxide-free distilled water. The strength of these solutions in terms of anhydrous citric acid by weight was determined by titration with 0.1 N sodium hydroxide solution which had been standardized with National Bureau of Standards benzoic acid according to directions furnished with the acid.

In making these analyses, a portion of the acid solution containing approximately 1.64 grams of anhydrous acid was weighed in a weighing bottle on the analytical balance, transferred to a 500-ml. volumetric flask, and diluted to the mark with boiled distilled water. Several 50-ml. aliquots of this final solution were titrated in 150-ml. Erlenmeyer flasks with 0.1002 N sodium hydroxide solution, using 3 drops of neutralized 1 per cent phenolphthalein solution as the indicator. About 25.5 ml. of sodium hydroxide solution were required to neutralize each portion.

As a further check, duplicate 1.64-gram portions of the citric acid dried to constant weight under vacuum at 60° C. were weighed out and made into 500 ml. of solution as described above. Portions of these solutions were titrated as above and it so happened that the average of the two determinations gave the exact theoretical value. (The error of a single determination was indicated as not greater than 1 in the third decimal place.)

The refractometer (Zeiss Abbe type with refractive index and sucrose scales) and the Brix spindles used in determining the soluble solids of the citric acid solutions were checked for accuracy. Boiled distilled water and solutions of highly purified moisture-free sucrose of 1, 5, 10, 20, and 30 per cent theoretical strength, respectively, were used in checking the refractometer. The Brix spindles were checked with solutions of pure sucrose at points on the scale coinciding very closely with those used with the citric acid solutions. These readings were made at 20° C. with the room temperature approximately the same.

Each of 24 citric acid solutions, varying in strength from 0.545 to 30.07 per cent, was checked with the refractometer and Brix spindle with results as shown in Table I. At least five readings were made on each of three or more portions, on two or more different days, with the refractometer, at 20° C. Duplicate checks of five readings each were made with the Brix spindle also at 20° C. The room temperature was 19° to 22° C. when most of the determinations were made.

The refractive indices were recorded to the nearest fourth decimal as indicated by the average reading. The sucrose values, based on Schonrock's data (1), were recorded as indicated by the average. The Brix values shown are the average of the different readings.

The values of Table I were plotted on a large-scale graph (20 mm. = 1 per cent on each ordinate) to obtain data for preparing a correction table. In the case of the refractometer data,

TABLE I. RELATIONSHIP OF TOTAL SOLIDS, REFRACTIVE INDEX, AND ° BRIX OF PURE CITRIC ACID SOLUTIONS

Anhydrous Citric Acid by Titration %	Refractive Index, 20° C.	Soluble Solids as Sucrose (1) %	° Brix, 20° C., by Hydrometer
0.000	1.3330	0.00	0.00
0.545	1.3337	0.48	0.61
1.007	1.3343	0.90	1.09
2.010	1.3355	1.77	2.17
3.021	1.3369	2.68	3.26
4.002	1.3381	3.52	4.32
4.904	1.3393	4.33	5.27
4.995	1.3394	4.42	5.38
5.805	1.3405	5.10	6.23
7.055	1.3421	6.20	7.27
7.701	1.3430	6.80	8.27
9.011	1.3447	7.92	9.63
9.674	1.3456	8.50	10.35
9.981	1.3460	8.76	10.67
10.96	1.3473	9.62	11.57
11.95	1.3487	10.50	12.75
13.42	1.3506	11.77	14.10
14.92	1.3527	13.10	15.90
18.19	1.3573	15.97	19.34
19.87	1.3596	17.40	21.00
22.08	1.3628	19.33	23.40
24.04	1.3656	21.06	25.40
25.94	1.3684	22.72	27.46
27.05	1.3701	23.68	29.00
30.07	1.3746	26.34	31.78



TABLE II. CORRECTIONS FOR OBTAINING ° BRIX OR ACTUAL SOLUBLE SOLIDS FROM REFRACTOMETER READINGS  
(Based on citric acid content of citrus juices or other acid-containing sugar solutions)

Citric Acid, Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value		Citric Acid, Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value		Citric Acid Anhydrous, % by Weight	Correction to Be Added to Refractometer Sucrose Value	
	To obtain ° Brix	To obtain true soluble solids		To obtain ° Brix	To obtain true soluble solids		To obtain ° Brix	To obtain true soluble solids
0.0	0.00	0.00	11.0	2.10	1.33	22.0	4.05	2.73
0.2	0.04	0.02	11.2	2.14	1.36	22.2	4.09	2.75
0.4	0.08	0.04	11.4	2.18	1.38	22.4	4.13	2.77
0.6	0.12	0.06	11.6	2.21	1.40	22.6	4.17	2.79
0.8	0.16	0.08	11.8	2.24	1.43	22.8	4.20	2.81
1.0	0.20	0.11	12.0	2.27	1.46	23.0	4.24	2.84
1.2	0.24	0.13	12.2	2.31	1.49	23.2	4.27	2.87
1.4	0.28	0.16	12.4	2.35	1.51	23.4	4.30	2.89
1.6	0.32	0.18	12.6	2.39	1.54	23.6	4.34	2.92
1.8	0.36	0.21	12.8	2.42	1.56	23.8	4.38	2.95
2.0	0.39	0.23	13.0	2.46	1.59	24.0	4.41	2.97
2.2	0.43	0.26	13.2	2.50	1.61	24.2	4.44	2.99
2.4	0.47	0.29	13.4	2.54	1.64	24.4	4.48	3.02
2.6	0.51	0.31	13.6	2.57	1.67	24.6	4.51	3.04
2.8	0.54	0.33	13.8	2.61	1.70	24.8	4.54	3.07
3.0	0.58	0.35	14.0	2.64	1.72	25.0	4.58	3.10
3.2	0.62	0.38	14.2	2.68	1.74	25.2	4.62	3.13
3.4	0.66	0.40	14.4	2.72	1.76	25.4	4.66	3.15
3.6	0.70	0.42	14.6	2.75	1.79	25.6	4.69	3.18
3.8	0.74	0.45	14.8	2.78	1.81	25.8	4.73	3.20
4.0	0.78	0.47	15.0	2.81	1.84	26.0	4.76	3.23
4.2	0.81	0.49	15.2	2.85	1.86	26.2	4.79	3.25
4.4	0.85	0.52	15.4	2.89	1.89	26.4	4.83	3.28
4.6	0.89	0.54	15.6	2.93	1.92	26.6	4.86	3.30
4.8	0.93	0.56	15.8	2.97	1.95	26.8	4.90	3.33
5.0	0.97	0.59	16.0	3.00	1.97	27.0	4.94	3.35
5.2	1.01	0.62	16.2	3.03	1.99	27.2	4.97	3.38
5.4	1.04	0.64	16.4	3.06	2.02	27.4	5.00	3.40
5.6	1.07	0.66	16.6	3.09	2.04	27.6	5.03	3.43
5.8	1.11	0.69	16.8	3.13	2.07	27.8	5.06	3.45
6.0	1.15	0.71	17.0	3.17	2.10	28.0	5.10	3.48
6.2	1.19	0.73	17.2	3.21	2.13	28.2	5.14	3.50
6.4	1.23	0.76	17.4	3.24	2.16	28.4	5.18	3.53
6.6	1.27	0.78	17.6	3.27	2.18	28.6	5.22	3.55
6.8	1.30	0.81	17.8	3.31	2.21	28.8	5.25	3.58
7.0	1.34	0.84	18.0	3.35	2.23	29.0	5.28	3.60
7.2	1.38	0.86	18.2	3.38	2.25	29.2	5.31	3.63
7.4	1.42	0.88	18.4	3.42	2.27	29.4	5.35	3.66
7.6	1.46	0.91	18.6	3.46	2.30	29.6	5.39	3.69
7.8	1.50	0.94	18.8	3.49	2.33	29.8	5.42	3.71
8.0	1.54	0.96	19.0	3.53	2.35	30.0	5.46	3.73
8.2	1.58	0.98	19.2	3.56	2.37	30.2	5.49	3.76
8.4	1.62	1.01	19.4	3.59	2.40			
8.6	1.66	1.03	19.6	3.63	2.43			
8.8	1.69	1.05	19.8	3.67	2.45			
9.0	1.72	1.08	20.0	3.70	2.47			
9.2	1.76	1.11	20.2	3.73	2.49			
9.4	1.80	1.13	20.4	3.77	2.52			
9.6	1.83	1.16	20.6	3.80	2.54			
9.8	1.87	1.18	20.8	3.84	2.56			
10.0	1.91	1.21	21.0	3.88	2.59			
10.2	1.95	1.24	21.2	3.91	2.62			
10.4	1.99	1.26	21.4	3.95	2.64			
10.6	2.03	1.28	21.6	3.99	2.67			
10.8	2.06	1.30	21.8	4.02	2.70			

the true per cent of anhydrous citric acid, as shown by titration, was plotted as ordinate against the corresponding refractometer sucrose value as abscissa. This resulted in practically a straight line and was plotted as such. The acid-degrees Brix relationship plotted in a similar manner gave a slight curve, bending upward. A 45° angle straight line was drawn to represent true or theoretical per cent of solids. This line fell between the other two but was nearer that of degrees Brix.

The data of Table II were obtained from this graph. This shows for each per cent of citric acid by titration the correction to be added to the corresponding refractometer sucrose scale reading to obtain the proper Brix value. Table II also includes a column of data for correcting refractometer sucrose scale values to true soluble solids or, in the case of pure acid solutions, the true per cent of acid, as would be shown by titration.

### Discussion

The use of the correction data of Table II is simple.

For example, a sample of lemon juice, containing 5.60 per cent of anhydrous citric acid by titration, may give a refractometer

sucrose scale or sucrose table value of 8.20. By referring to the table the correction to be added for 5.60 per cent acid is found to be 1.07, when it is desired to correct the refractometer reading to degrees Brix. The approximate Brix value of the juice is, thus, 8.20 + 1.07 or 9.27. If it is desired to correct the refractometer reading to true per cent of soluble solids, the correction is 0.66 and the final corrected value becomes 8.20 + 0.66 or 8.86.

Table II may also be used to correct Brix readings to true solids when the acid content is known by subtracting the corresponding correction in the second column and adding that in the third column.

Tests made with solutions containing both citric acid and sucrose verified the corrections for acid shown in Table II.

In general the corrected refractometer sucrose values on citrus juices are slightly lower than the corresponding Brix spindle values.

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# Change in Solvency during Evaporation of Thinners

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A rapid film evaporator for "mineral spirits" and related naphthas permits the measurement of change in solvency of hydrocarbon thinner blends as 100 ml. are evaporated in the form of a film during less than 3 hours at room temperature.

**O**LEORESINOUS protective coatings are frequently cut hot with a high-solvency naphtha and later thinned with a material of considerably lower solvency—e. g., "mineral spirits." When a difficultly soluble resin forms a part of the coating, it is important that solvency should not fall away too rapidly during application and setting. Maintenance of solvency during evaporation also makes possible a better leveling of the film and generally improves the physical characteristics of the coating.

An apparatus has been devised wherein 100 ml. of a thinner or a mixture of thinners, which boil within or near the mineral spirits boiling range, can be evaporated in less than 3 hours, at room temperature, and as a film. Characteristics of the evaporation differ from those accompanying actual coating application in two respects—viz., the film is in motion, and no nonvolatile component is present.

A number of evaporation methods whereby changes in solvency during evaporation can be determined have been described (1, 4, 6-8). Most were designed to deal with lacquer thinners, and have provided for evaporation and sampling from pools of liquid contained in a beaker, paint-can cover, or crystallizing dish. When comparatively high-

boiling materials, such as mineral spirits, are evaporated from pools in sufficient quantity for sampling during the progress of the evaporation, too much time is required. Further, it seems reasonable that evaporation as a film should more nearly simulate actual conditions than evaporation from a pool, in some cases inches deep.

During the setting and drying of a protective coating film the effect of solvent retention occurs. Dorsch and Stewart (3)



FIGURE 2. APPARATUS

have shown that the retention of hydrocarbons by nitrocellulose films differs from retention of esters and alcohols of the same evaporation rate. For most oleoresinous and synthetic resinous coatings, however, hydrocarbons alone are employed as thinners, and thus the error introduced by the total absence of nonvolatile vehicle may be assumed to be fairly constant and of lower magnitude in the case of mineral spirits than with lacquer volatiles.

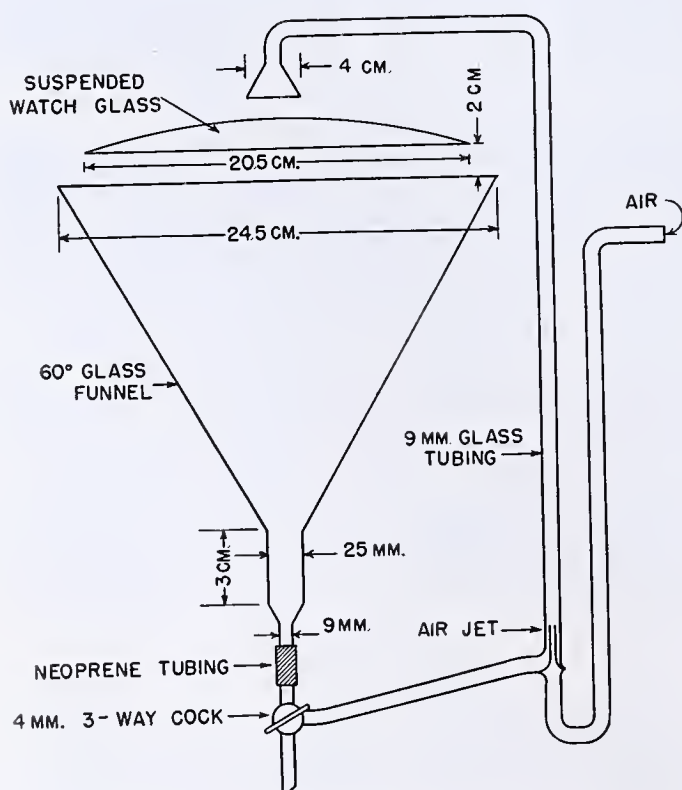


FIGURE 1. SOLVENT FILM EVAPORATOR



Estimation of Solvency

A convenient method of determining solvency as the thinner evaporates is to abstract small samples (1 ml.) after one half, three quarters, and seven eighths are off, and take the aniline points. Aniline point is so generally accepted as a measure of solvency of a hydrocarbon thinner of a given boiling range that several large producers and consumers of naphthas use it as a specification solvency test. It requires neither temperature control nor costly equipment.

To abstract three 1-ml. samples, and yet not greatly upset the composition of the fractions, it is desirable to evaporate 100 ml. of naphtha.

Since most oleoresinous or resinous coatings retain considerable thinner after reaching their set point (2), no measurements of a residual portion less than one eighth were taken.

Precision of Method

The precision attainable in the apparatus was originally tested by making two runs with the same thinner mixture under different conditions. Run 1 was made with 200 ml. during 207 minutes for seven eighths evaporated, and in a steam-heated room without other temperature or humidity control. Run 2, and subsequent runs detailed below, were made with 100 ml., in about half the time (112 minutes for seven eighths evaporated in run 2), in a room maintained at 25° C. and 50 per cent relative humidity. That time and temperature, within fairly narrow limits, were not factors affecting the operation of the apparatus is indicated in Table I. Thinner mixture, of 31.4° C. aniline point, was blended from two volumes of Stoddard solvent and one volume of No. 2 aromatic naphtha (Table III).

The rate of evaporation is not considered. The method is limited to the determination of change in solvency during evaporation at a speed of the same order of magnitude as that encountered in the setting of oleoresinous varnishes and enamels.

TABLE I. ANILINE POINTS

	Last Half ° C.	Last Quarter ° C.	Last Eighth ° C.
Run 1	47.2	55.5	61.0
Run 2	47.6	55.8	61.0

Apparatus

It may be found convenient to modify the apparatus (Figures 1 and 2), but the present setup is quickly assembled, sufficiently rapid for most purposes, and automatic. The small glass-sealed air jet may be replaced by a Neoprene-connected T-tube arrangement. The funnel need not necessarily be of glass, although liquid level reading is thus facilitated. The flared overhead discharge tube should be large enough, and close enough to the watch glass, to prevent spattering as the bubbles break. The fan should be

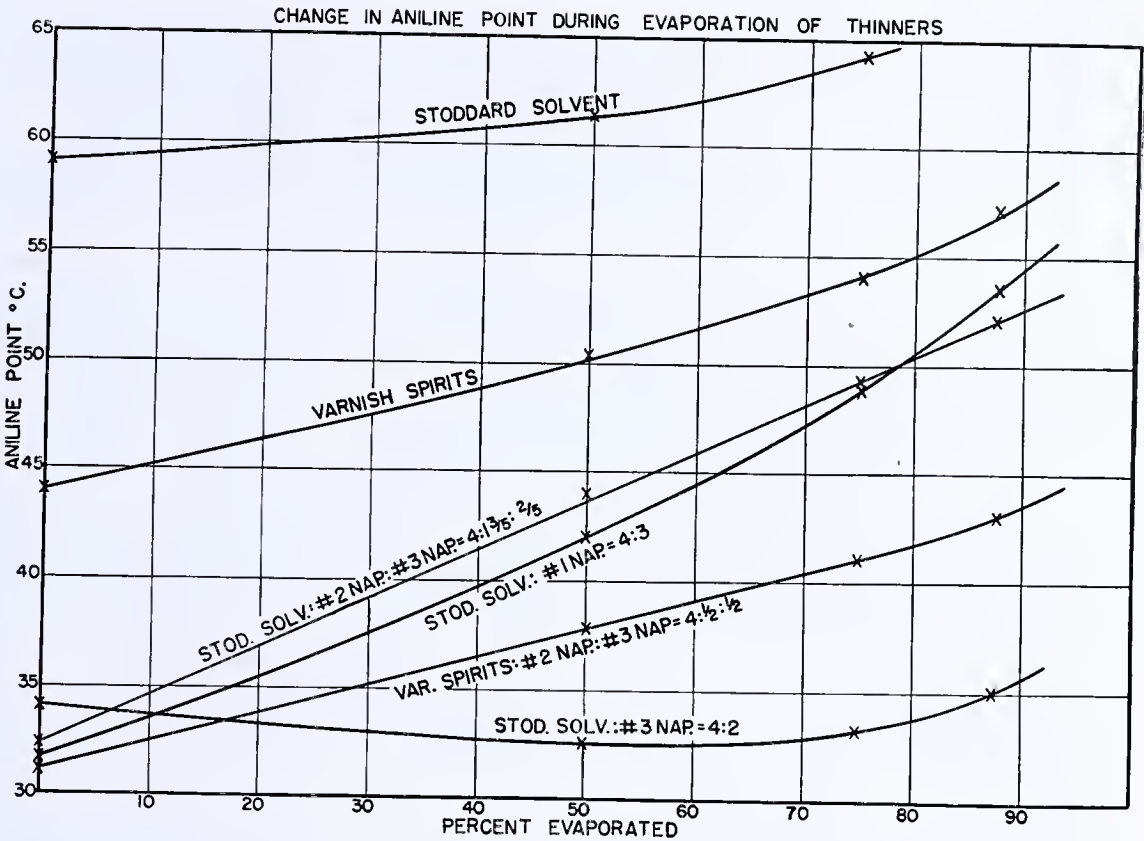


FIGURE 3

TABLE II. ANILINE POINTS

Thinner or Blend	Original ° C.	Last Half ° C.	Last Quarter ° C.	Last Eighth ° C.
Stoddard solvent	58.0	61.3	64.2	66.0
Varnish spirits	44.0	50.4	54.0	57.2
Stoddard solvent, 4 volumes No. 1 naphtha, 3 volumes	31.6	42.0	48.9	53.7
Stoddard solvent, 4 volumes No. 3 naphtha, 2 volumes	34.0	32.6	33.3	35.1
Stoddard solvent, 4 volumes No. 2 naphtha, 1.6 volumes No. 3 naphtha, 0.4 volume	32.4	44.0	49.0	52.2
Varnish spirits, 4 volumes No. 2 naphtha, 0.5 volume No. 3 naphtha, 0.5 volume	31.4	37.9	41.1	43.2

TABLE III. INSPECTIONS

	Stoddard Solvent	Varnish Spirits	Aromatic Naphtha		
			No. 1	No. 2	No. 3
Gravity, ° A. P. I.	49.4	45.6	35.9	33.6	29.8
Specific gravity	0.782	0.799	0.845	0.857	0.877
Initial boiling point, ° C.	155	154	133	131	175
5% off	162	159	142	137	178
10%	163	161	143	139	180
50%	172	170	152	147	186
90%	192	185	171	163	197
95%	201	191	177	169	202
Dry point	208	202	183	176	210
Final boiling point, ° C.	210	202	184	177	210
Tag closed-cup flash, ° C.	41	41	28	29	55
Mixed aniline point, ° C. <sup>a</sup>	...	...	28.0	17.6	22.4
Aromatics, %	...	...	73.5	91.8	89.2

<sup>a</sup> A control test now run in several laboratories, measuring the critical solution temperature of a mixture of 10 ml. of anhydrous aniline, 5 ml. of sample, and 5 ml. of any naphtha whose aniline point is 60° C.  
<sup>b</sup> As determined by method of Philadelphia Paint and Varnish Production Club (5).

of such power and distance from the apparatus (20 cm. in the present instance) that no droplets of liquid are carried away. An air current which requires only a 2° or 3° tilt of the watch glass toward the fan for equal film distribution over the surface appears to be satisfactory. The lower speed of a conventional rubber-bladed automobile defrosting fan is used in this laboratory. Air current should be directed underneath the watch glass, to scavenge vapors inside the funnel, as well as above. The funnel is graduated, with the fan shut off, while the air lift is in operation. Liquid holdup of the apparatus as shown amounts to 9.5 ml.



### Operation

Air from the laboratory line is admitted before the 100 ml. of thinner are poured into the funnel. The air lift is regulated, conveniently with the aid of a constant-pressure by-pass, to supply a smooth, equally distributed flow of bubbles. After the first three quarters of the thinner have evaporated it may be necessary to increase the air slightly, owing to loss of liquid head.

When the 50-ml., 25-ml., etc., marks have been reached, a few milliliters are run out into a small beaker and 1 ml. is pipetted into a test tube which is corked tightly. The remainder is poured back into the funnel at once. Aniline points, using equal volumes of thinner sample and anhydrous aniline, were taken at the end of each run and read to 0.1° C. with the same thermometer.

### Fractional Solvencies

Table II lists solvencies of fractions remaining from the evaporation of two typical mineral spirits, and of several

blends of these with commercial high-solvency naphthas. The solvency corresponding to an aniline point of about 32° C. was taken as typical of that of the total thinner present in many current industrial oleoresinous finishes. Figure 3 illustrates the changes in solvencies.

Table III shows pertinent inspections of the commercial thinners used.

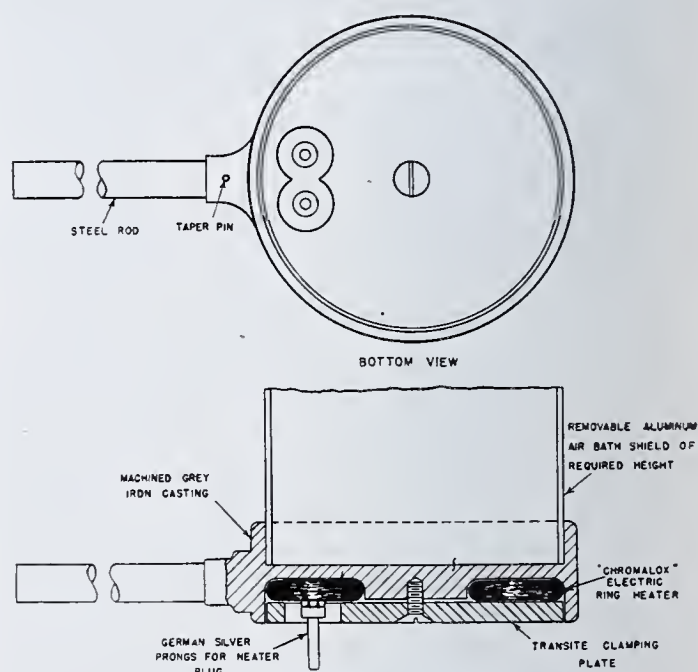
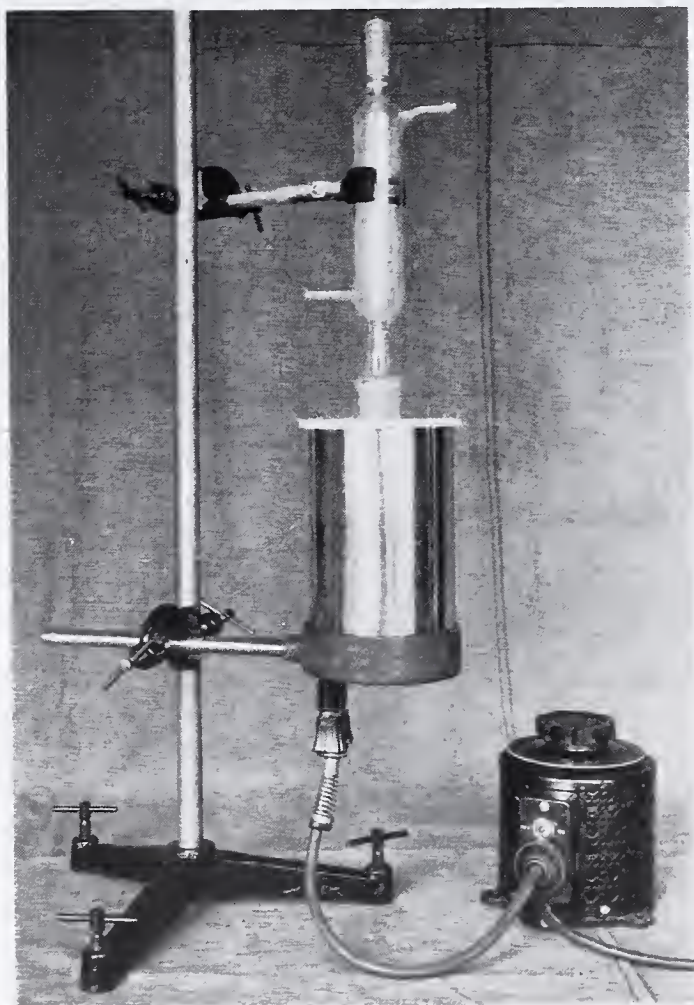
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## A New Style of Chemical Heater

W. MASTER, Consolidated Edison Company of New York, Inc., Brooklyn, N. Y.

A NEW style of electric heater, developed several years ago by the Research Bureau of the Consolidated Edison Company, has proved very satisfactory in severe chemical laboratory service. It may be used as an ordinary hot plate or as an "air bath" when provided with a removable heat-reflecting jacket. In the latter form, shown in the photograph,



it is an excellent substitute for water, oil, or glycerol baths with the added advantage of eliminating liquids. Under ordinary conditions the air-bath temperature may be maintained within a few degrees by means of a rheostat, transformer, or thermostat. In a draft-free location or by the use of a double jacket, regulation within a fraction of a degree is possible. It is exceptionally rugged and to date no trouble has been experienced from corrosion so frequently encountered in chemical heaters.

Various sizes may be made using stock heating units. The diagram shows the construction of a good general-purpose heater built around a 500-watt Chromalox A-20 ring unit. This type of unit is inherently resistant to corrosion and is further protected from spilled chemicals by the lip around the bottom of the casting and the transite clamping plate which holds it in intimate contact with the casting. Prongs of nickel silver are substituted for the wire-holding nuts on the unit, care being taken not to disturb the nuts next to the sheath. The holding rod is 18-8 stainless steel 0.5 inch in diameter and the jacket is anodized 2S aluminum alloy tubing of 4-inch diameter.



# Permeability to Moisture of Organic Surface Coatings

## Use of Glass Cloth in Permeability and Adsorption Measurements

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A GREAT deal of excellent work has been done on the permeability of various films and coated fabrics to moisture, organic liquids, and several gases (3-7, 12, 13, 15, 19, 22, 23, 31). The data obtained from this work have furnished considerable evidence in support of the theory regarding the mechanism by which permeation takes place. These data have shown the phenomenon to be a complex physico-chemical process, affected by the vapor pressure differential across the film, the relative polarity and solubility of film and vapor, film structure and its resistance to imbibition forces, as well as the physical dimensions of area and film thickness.

The data have also shown that all organic films are permeable to moisture. The permeability will vary from an extremely small amount through such nonpolar films as paraffin wax and rubber (20, 21, 29, 30) to a relatively large quantity through such a film as raw linseed oil.

In general, the moisture adsorption of a coating is related to its permeability, but there are many exceptions to this. For example, a short oil-limed rosin varnish will have a high moisture adsorption but a fairly low permeability, but the most striking contrast may be found in shellac which has a very high moisture adsorption and surprisingly low permeability (8, 9, 20, 21). These variations in permeability and moisture adsorption, together with the demand for high water resistance in surface coatings, have made necessary more precise methods for measuring the water sensitivity of a coating under all possible conditions. This has resulted in a technique which will measure the time required for moisture to permeate a film—the actual amount of water which will pass through a film under specified conditions, and the amount of water which will be adsorbed by the film.

Specific methods are available for certain industries, types of film, or materials to be coated. For example, the time required for electrical breakdown of a film under constant potential and varying humidity conditions is taken as a measure of the permeability of the film in the electrical insulating industry (1, 11). The Forest Products method (2) uses the time rate of increase in weight of coated wooden panels subjected to specific humidity conditions to indicate the permeability of the coatings to moisture. A method which has a much more general applicability is the Gardner jar method or one of its many modifications as used by Muckenfuss (16), Gettens (10), Payne and Gardner (21), the New Jersey Zinc Co. (14), the Bell Telephone Laboratories (29, 30), the New York Paint and Varnish Production Club (17), and many others.

At the convention of the Federation of Paint and Varnish Production Clubs in Cincinnati in 1937 the New York club proposed a standard method for permeability measurement. The method measures the rate at which moisture will pass through a film under specific conditions of vapor pressure differential, temperature, and area of film. Using a specially designed metal cup, known as the Payne

permeability cup (Figure 1), it was shown that check results could be obtained with this method by operators working in different laboratories, and that a support could be used on which to apply the film-forming material. This avoids the rather unsatisfactory procedure of making free films for testing, and permits the permeability measurement of films of brittle or weak materials which could not be prepared as free films. The material used by the New York club for the film support was the parchmentized paper known as "Patapar." This material gave excellent results when used with flexible air-drying coatings, but some slight difficulty was encountered with brittle materials and it was not satisfactory for baking materials or for exterior exposure tests. This was due to the fact that the small percentage of moisture present normally in the Patapar was lost under the conditions of baking and was regained with subsequent exposure to laboratory conditions. The variation in moisture content produced variation in volume of the Patapar with consequent distortion of the film it was supporting.

The purpose of the present paper is to show that a fine grade of glass cloth may be used as the support for films intended for permeability and adsorption measurements. This support does not change in volume in contact with moisture, and it may be used satisfactorily at the baking temperatures required in the surface coating industry.

### Glass Cloth

The glass cloth used was obtained from the Owens-Corning Fiberglas Corp., Toledo, Ohio, and is known as Fiberglas Cloth No. 01-175. It is described as follows:

Specific gravity, 2.60 ounces per square yard  
Thickness, 0.003 inch  
Thread size, warp 900-2/2, filling 900-1/2  
Number of threads per inch, warp 60, filling 64

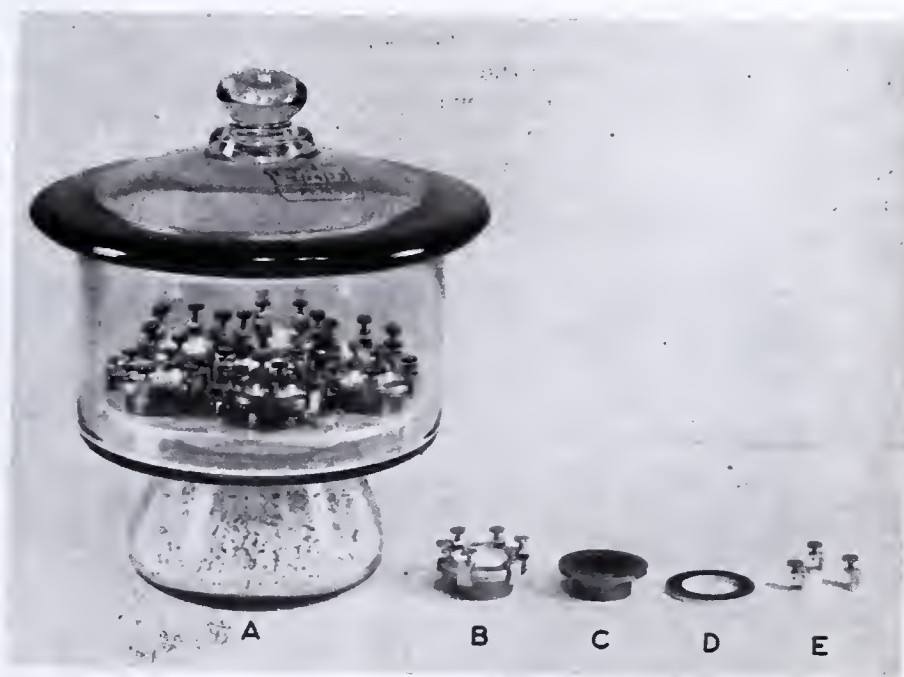


FIGURE 1. PERMEABILITY APPARATUS

A. Desiccator with cups  
B. Payne permeability cup, loaded  
C. Cup  
D. Flange  
E. Clamps



The material is made from a glass composition which possesses excellent electrical properties because it is intended for electrical use, but it is not sufficiently resistant to chemical attack for use in contact with corrosive chemicals.

The difference in structure of glass cloth and Patapar is shown clearly in Figures 2 and 3. The individual filaments of the glass cloth are very fine, but a number of them are twisted together to form a thread. The threads are woven in the normal manner with the warp running the length of the cloth and the filling across the cloth. There are small regular

Any of the standard application methods may be used to apply the film-forming material to the glass cloth, but the most satisfactory procedure is to apply the first coat by dipping the glass cloth into the material and allowing it to drain and dry in the normal manner. Subsequent coats may be applied by brushing, spraying, or dipping. If the first coat must be applied by spraying or brushing, a very satisfactory holder may be made by cutting the rim off a 1-gallon triple-seal friction-top paint can and also cutting out the metal from the lid of the same can, leaving the rim of the lid only.

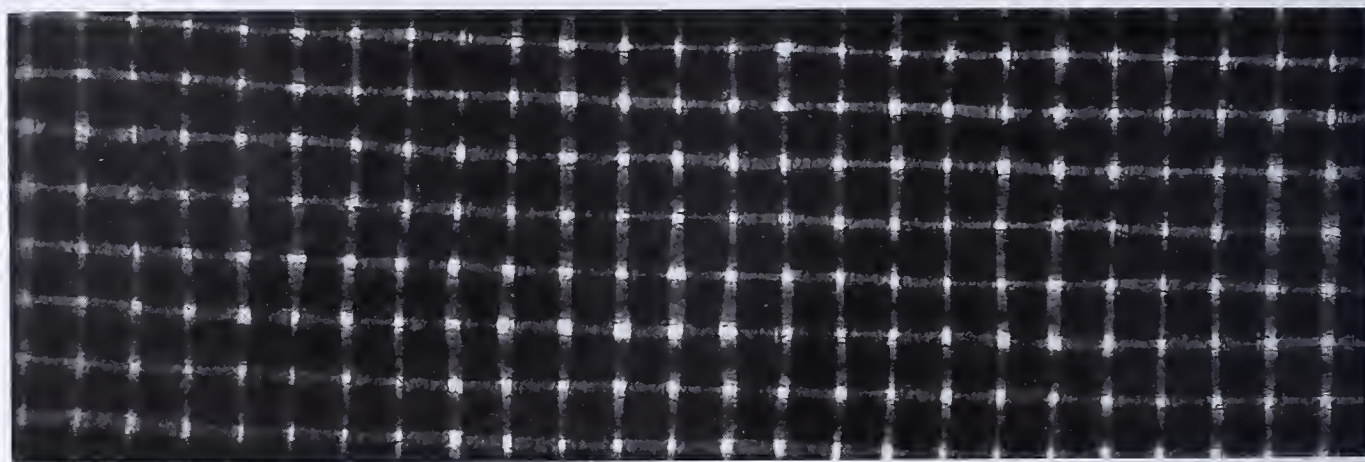


FIGURE 2. GLASS CLOTH BY TRANSMITTED LIGHT ( $\times 15$ )  
Dark sections, threads. Light sections, spaces between threads

spaces at the intersections of the threads, as shown by transmitted light in Figure 2. The Patapar has a matted structure with interstitial spaces of irregular dimensions distributed throughout its mass. Figure 3 shows the spaces in the Patapar to be smaller than those in the glass cloth but this does not affect the rate of moisture movement through it, as shown in Table I.

TABLE I. MOISTURE LOSS

	Gram/hr.
Open cup	0.0830
Patapar	0.0625
Glass cloth	0.0618
Film A	0.0014
Film E	0.0002

The rate of moisture loss from an open cup was compared with the rate from cups covered with Patapar, glass cloth, and films of materials A and E under the same conditions as those used in the permeability determinations.

Table I shows that the Patapar and glass cloth retard the loss of water to about the same extent, but that the rate of moisture movement through these materials is so large compared with the rate of typical surface coatings that the effect on permeability values would be insignificant.

If the glass cloth is placed between the two rims and the rim from the lid forced into position, the glass cloth will be drawn tight and held very firm, but care must be taken to adjust the material and spray conditions so that a continuous coating is formed free from pinholes.

The glass cloth is wetted easily by surface coatings, but Figure 2 shows the possibility of pinhole formation at the intersections of the threads. This is eliminated entirely when the glass cloth is dipped into the coating, as shown in Figure 4, by the excellent penetration of the coating into the cloth.

The photomicrograph of the cross section of glass cloth which has been coated on both sides shows the ends of two warp threads with their individual filaments embedded in the coating with very few voids, and a filling thread running under one warp and over the other in intimate contact with the coating over its entire length. In contrast to this the coated Patapar, Figure 5, shows the two films in contact with the Patapar at isolated places only, with considerable voids between the Patapar and the film and no penetration of the film material into the Patapar. Water permeating through this structure could accumulate in the voids and saturate the

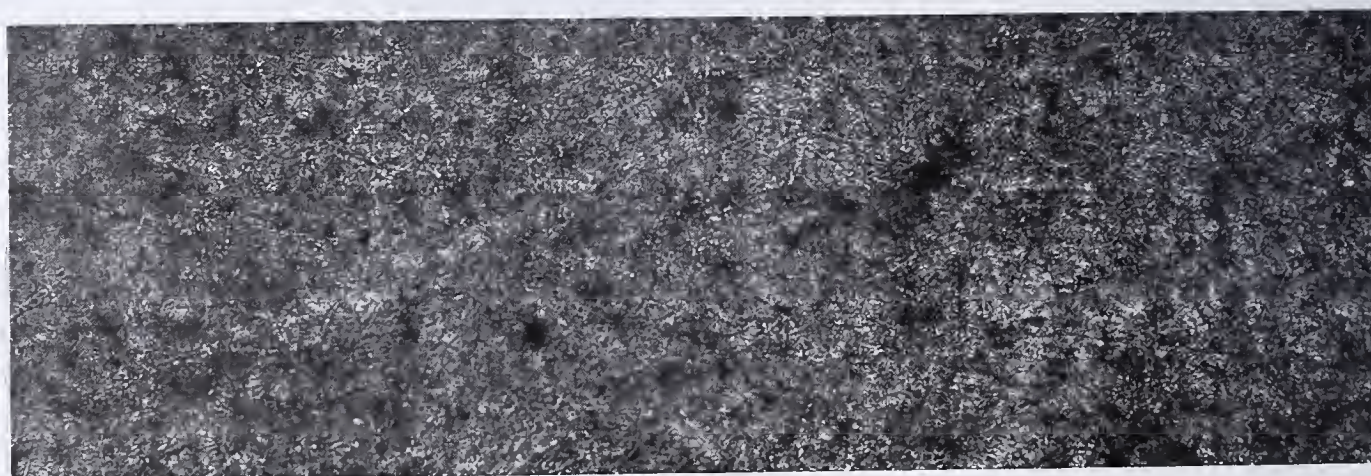


FIGURE 3. PATAPAR BY TRANSMITTED LIGHT ( $\times 15$ )



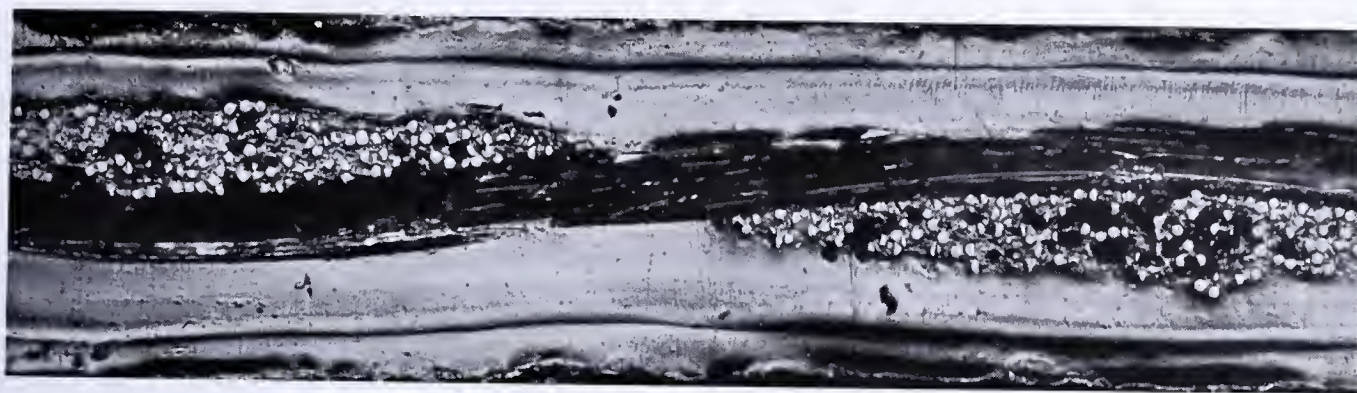


FIGURE 4. GLASS CLOTH, COATED ON BOTH SIDES (CROSS SECTION,  $\times 250$ )

Patapar, with subsequent swelling and distortion of the films and increase in permeability. This condition is avoided in the New York club method by coating only one side of the Patapar.

The film thickness on the Patapar is apparently more uniform than on the glass cloth, but the almost complete penetration of the cloth by the film ensures a film uniformity not apparent from the photomicrograph. The coated cloth is practically a solid film reinforced with glass fibers. In this respect it approaches more nearly its condition on a metal

The thickness of the film on glass cloth is calculated by the same procedure (weight-area-specific gravity relationship) as used in the New York club method. It is recognized that there is a variation in film thickness due to the woven structure of the glass cloth and this is shown clearly in Figure 4, but permeability has been shown to be inversely proportional to film thickness over the range of thickness in question; therefore, there would be no discrepancy in the calculation of specific permeability from an average value of film thickness. The coated glass cloth is practically a solid film reinforced

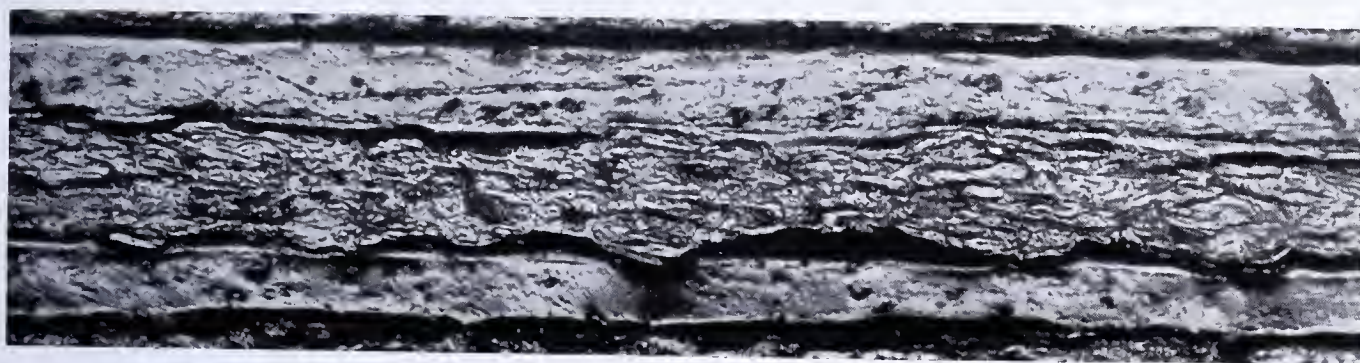


FIGURE 5. PATAPAR, COATED ON BOTH SIDES (CROSS SECTION,  $\times 250$ )

panel, although the orientation at the film-glass interface would differ slightly from the orientation on metal. The film on Patapar is more nearly like a free film.

### Permeability Measurement

The New York Paint and Varnish Production Club standard method (17) was used for permeability measurement, but glass cloth was substituted for the Patapar.

The film-forming materials under investigation are applied to one side of the Patapar support by any of the general methods—brush, spray, or flow on—but not by dipping because both sides of the Patapar must not be coated. The film is allowed to dry on the support for any specified length of time and a disk is then cut from it. A similar disk is cut from the uncoated Patapar, both are weighed, and the difference is the weight of the film on the Patapar. The thickness of the film may be calculated from its weight, area, and specific gravity. The coated disk is placed between the flanges of a Payne permeability cup after about 5 grams of water have been placed in the cup. The flanges are then clamped together tightly and the loaded cup is weighed and placed in a desiccator with phosphorus pentoxide as the desiccant. The desiccator is kept in an oven maintained at  $38^{\circ}\text{C}$ . ( $100^{\circ}\text{F}$ .) and the cup is weighed periodically to determine the amount of water which has permeated through the 10 sq. cm. area of film.

The dimensions of the Payne cup are such that the specific permeability rating may be obtained simply by multiplying the loss in weight from the cup in grams by 100 and by the film thickness in millimeters if the weighings are made each 24 hours. The specific permeability is defined as the milligrams of water permeating through 1 sq. cm. area of film of 1-mm. thickness in 1 day under specified conditions of temperature ( $38^{\circ}\text{C}$ .) and vapor pressure differential.

with glass fibers and the difference in weight of uncoated and coated glass is the weight of the coating which may be converted into thickness from the relationship existing between specific gravity and area.

A series of tests was made, with the above method, to determine the relation between Patapar and glass cloth, using the following materials:

A. CLEAR FLEXIBLE COATING. Rezyl resin<sup>1</sup> 869-1 with cobalt drier.

B. CLEAR BRITTLE COATING. Orange shellac.

C. SHORT OIL-PHENOL MODIFIED RESIN VARNISH. Phenac resin<sup>2</sup> 622N, 100; tung oil, 80; mineral spirits, 170 parts by weight. Heat-processed in the normal manner and thinned with mineral spirits.

D. NITROCELLULOSE LACQUER. Nitrocellulose, 0.5 second, 100; Rezyl resin<sup>1</sup> 99-4, 100; and dibutyl phthalate, 20 parts by weight on the solid basis. Thinned with appropriate solvents.

E. WHITE BAKING PRIMER. Titanium dioxide, 80; zinc oxide, 80; and Rezyl resin<sup>1</sup> 412-1 (50% solids), 200 parts by weight. Mineral spirits to correct viscosity.

F. WHITE BAKING ENAMEL. Titanium dioxide, 97; zinc oxide, 3; and Beetle resin<sup>2</sup> 592-8 (50% solids), 200 parts by weight. Xylene to correct viscosity.

Patapar No. 30, Paterson Parchment Paper Company, Bristol, Penna.

Fiberglass Cloth No. 01-175, Owens-Corning Fiberglass Corp., Toledo, Ohio.

Payne permeability cup, R. P. Cargille, New York, N. Y.

<sup>1</sup> Registered trade-mark of the American Cyanamid Co.

<sup>2</sup> Trade-mark of the American Cyanamid and Chemical Corp.



## Comparison of Patapar and Glass Cloth

A comparison was made of the permeability of four typical air-drying surface coatings, A, B, C, and D, on Patapar and on glass cloth. Two coats of each material were applied as shown in Table II, and each coat was air-dried for one week.

TABLE II. COMPARATIVE PERMEABILITY

Material	Method of Application	Specific Permeability	
		Patapar	Glass cloth
A	Dip, both sides	1.370	0.868
	Flow, one side	0.813	0.835
	Spray, one side	0.830	0.876
B	Dip	0.510	0.292
	Flow	0.310	0.298
C	Dip	0.598	0.243
	Flow	0.306	0.212
D	Dip	1.091	0.872
	Flow	0.890	0.884

In each case where the material was applied by dipping and thereby coating both sides, the permeability on the Patapar was higher than on the glass cloth. The permeability readings for the same material on Patapar and glass cloth check satisfactorily when only one side of the Patapar was coated. The high permeability reading on the Patapar was caused by adsorption of water by the layer of Patapar between the two layers of coating. The adsorbed water swelled the Patapar and distorted the film, producing minute cracks in brittle materials and weak places in flexible materials. The large increase in area of the film on Patapar was apparent from its wrinkled appearance, while the film on the glass cloth was perfectly smooth and unaffected.

These results show that the same permeability values may be obtained for films on Patapar or on glass cloth, but that the glass cloth is not subject to the limitation of being coated on one side only.

## Glass Cloth for Baking Materials

To illustrate the value of the glass cloth as a support for baking coatings, the permeabilities of the white baking primer, E, and the white baking finish enamel, F, were determined. The results are shown in Table III.

The physical characteristics of a baking coating vary with the time and temperature of the bake, and it is desirable to determine the minimum schedule consistent with optimum characteristics such as color, gloss, hardness, and chemical and water resistance. The permeability and water adsorption of the baked film are indications of its water resistance. The variation in permeability of the white baking enamel, F, with variation in baking schedule is also shown in Table III.

TABLE III. PERMEABILITY OF WHITE BAKING COATINGS

Material	Bake Hour	° F.	Specific Permeability
E	0.75	350	0.116
1 coat E	0.75	350	0.103
1 coat F	1	275	
F	1	225	0.276
	1	275	0.113
	0.5	325	0.108
	1	325	0.084

The permeability determinations were all run in duplicate with results which did not vary more than  $\pm 1.5$  per cent. It is apparent from the above values that glass cloth is a very satisfactory support for permeability determinations on films of materials which require baking at elevated temperatures.

It is also apparent that permeability determinations may be used to indicate the baking schedule required to give a material the necessary degree of water resistance. These values check very nicely the water adsorption results obtained on these same films as described below. The best method of applying the film-forming material to the glass cloth is to dip the first coat; the succeeding coats may be dipped, sprayed, or brushed.

## Water Adsorption

The time required and the extent to which a film structure will adsorb water are indications of its water resistance. The adsorption is not necessarily proportional to the degree of softening and whitening of the film when immersed in water, nor to the permeability of the film, but it serves a useful purpose in the evaluation of a surface coating.

The McBain-Bakr quartz fiber spring balance (18) may be used to determine adsorption-desorption isotherms with extreme precision over a wide range of relative humidities, but a simple water immersion test with periodic weighings will determine very satisfactorily the amount of water taken up by a film under this condition.

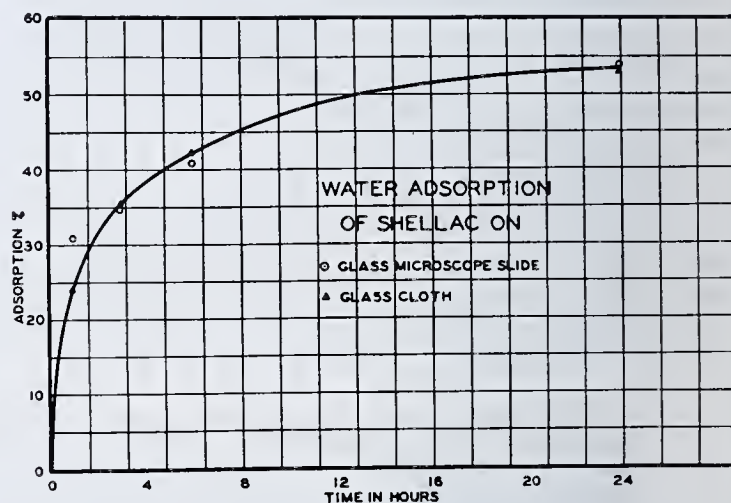


FIGURE 6

The British Ministry microscope slide test for water adsorption specifies that a glass slide be dipped into the material being tested and, after proper drying of the film, the coated slide immersed in water. The slide is weighed before and after coating and after immersion, and the gain in weight is expressed as per cent water adsorbed by the film. The glass slide is better than a metal panel because of the absence of corrosion, but it has some disadvantages. Materials, such as nitrocellulose lacquers, lose their adhesion to the slide after a short period of immersion and cannot be handled satisfactorily. In some cases where the material is fairly water-sensitive the water tends to accumulate in blisters between the slide and the coating and it is very difficult to remove this water without disrupting the film. The test requires that all surface adhering water be removed, so that only the water adsorbed by the film shall be weighed, but it is obviously impossible to remove a thin layer of water which may be between the film and the glass slide. The disadvantages of the glass slide are overcome entirely by the use of glass cloth. There is no loss of adhesion because the coating is enmeshed completely in the fibers of the cloth, and there is also no possibility of forming blisters underneath the coating. The water adhering to the surface is removed easily by placing the wet coated cloth between heavy blotting paper, but care should be taken to make the time required for weighing the sample uniform, so that the surface water only and no adsorbed water will be lost.

The water adsorption of a number of materials on glass slides and on glass cloth was compared and in every case the results were found to check satisfactorily.

Table IV and Figure 6 show the water adsorption of shellac. The mechanism of adsorption is not simple diffusion in the film (24-28) or it would be represented by some form of Fick's diffusion law

$$X = D \frac{(C) \text{ time}}{\text{thickness}}$$



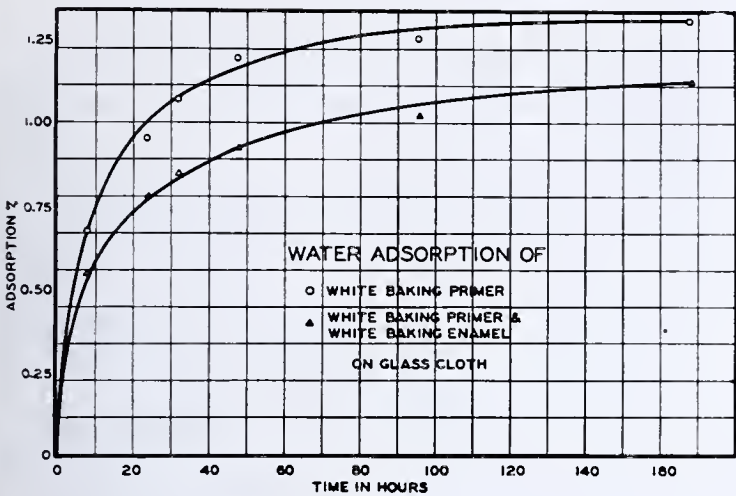


FIGURE 7

where  $X$ , the amount of water diffusing, is directly proportional to  $D$ , the diffusion constant for the particular material,  $C$ , the concentration, and the time, and inversely proportional to the film thickness. This law states that the amount diffusing is a linear function of the time, but the curve is parabolic, showing that both film structure and simple diffusion are factors in this phenomenon.

TABLE IV. WATER ADSORPTION OF SHELLAC

Hours	Microscope Slide			Glass Cloth		
	Film 1, 0.0954 g.	Film 2, 0.0921 g.	Av., 0.0937 g.	Film 1, 0.1018 g.	Film 2, 0.1051 g.	Av., 0.1035 g.
1	30.2	31.8	31.0	23.8	25.0	24.4
3	34.2	35.4	34.8	35.1	36.1	35.6
6	40.1	41.3	40.7	41.8	42.6	42.2
24	53.4	54.4	53.9	52.7	53.5	53.1

Another distinct advantage of the glass cloth over the glass slide is the fact that permeability and adsorption may be determined on the same strip of film. This ensures identical application, film thickness, and conditions of drying, all of which are important factors in these determinations or in establishing any relationship between them.

A strip of glass cloth was dipped in the white baking primer,  $E$ , and baked as shown in Table V; then a coat of the baking enamel,  $F$ , was sprayed on one side of the primed cloth and baked as shown. The coated glass cloth had practically the same appearance as a metal panel finished in the same manner, very good gloss, color, and hardness. Disks were cut from the coated cloth and permeability measurements made as shown previously, and strips the size of a microscope slide ( $7.5 \times 2.5$  cm.,  $3 \times 1$  inch) were also cut and the water adsorption determinations made.

TABLE V. WATER ADSORPTION OF WHITE BAKING PRIMER AND ENAMEL

Hours	Primer Bake 0.75 Hour at 177° C. (350° F.)			Enamel Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.2253 g.	Film 2, 0.2168 g.	Av., 0.2110 g.	Film 1, 0.4295 g.	Film 2, 0.4283 g.	Av., 0.4289 g.
8	0.69	0.66	0.675	0.52	0.58	0.55
24	0.95	0.96	0.955	0.76	0.79	0.775
32	1.09	1.05	1.07	0.82	0.86	0.84
48	1.26	1.18	1.22	0.90	0.93	0.915
96	1.25	1.25	1.25	1.03	1.01	1.02
168	1.33	1.29	1.31	1.12	1.12	1.12

The same shaped curve was obtained as with the shellac, but of course on a very different scale. The curve for the primer and enamel shows a lower adsorption than for the primer alone, owing to the additional baking period on the primer while the enamel was being baked over it and to the excellent water-resisting characteristics of this combination.

Variation of Water Adsorption with Baking Schedule

It was shown in Table III that the permeability of films baked at different times and temperatures could be used to determine the optimum baking schedule for the characteristics desired. Table VI and Figure 8 indicate that adsorption determinations may be used for the same purpose or as a check on the permeability results.

TABLE VI. VARIATION IN WATER ADSORPTION WITH BAKING CONDITIONS

Hours	(White baking enamel) Bake 1 Hour at 107° C. (225° F.)			Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.6157 g.	Film 2, 0.5982 g.	Av., 0.6069 g.	Film 1, 0.5180 g.	Film 2, 0.5162 g.	Av., 0.5121 g.
8	0.88	0.92	0.90	0.82	0.71	0.765
27	1.22	1.34	1.28	1.03	0.93	0.98
48	1.42	1.50	1.46	1.03	1.01	1.02
72	1.48	1.52	1.50	1.04	1.02	1.03
Hours	Bake 0.5 Hour at 163° C. (325° F.)			Bake 1 Hour at 163° C. (325° F.)		
	Film 1, 0.5513 g.	Film 2, 0.5395 g.	Av., 0.5454 g.	Film 1, 0.5109 g.	Film 2, 0.4975 g.	Av., 0.5042 g.
8	0.72	0.72	0.72	0.64	0.65	0.645
27	0.89	0.91	0.90	0.68	0.74	0.71
48	0.92	0.92	0.92	0.73	0.75	0.74
72	0.93	0.95	0.94	0.75	0.77	0.76

The same strip of coated cloth was used for determining both permeability and adsorption. The results check except for a reversal of  $X$  and  $Y$ , but this might be expected from the closeness of the figures and in view of the fact that permeability and adsorption are not necessarily directly proportional to each other. The results affirm the fact that, within limits,

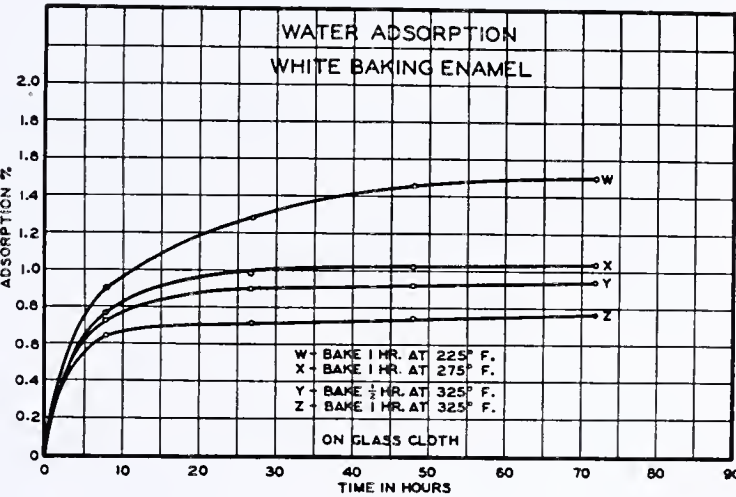


FIGURE 8

an increase in time or temperature of baking will increase the resistance of a film. This is shown even more emphatically in the following section.

Alcohol Adsorption

The permeability and water adsorption results shown in Tables III and VI were used to indicate the optimum baking schedule necessary for water resistance, and it will be seen from Table VII and Figure 9 that adsorption of liquids other than water may be used for this same purpose. The advantage of being able to cut portions from the same strip of coated glass cloth for these various determinations will be apparent.

The shape of the curves obtained from the adsorption of alcohol is not the same as those obtained from water. This is no doubt due to incomplete conversion of the film at the  $X$  baking schedule; the film still retained a small proportion of alcohol-soluble material which was leached out by the alcohol with consequent loss in weight.



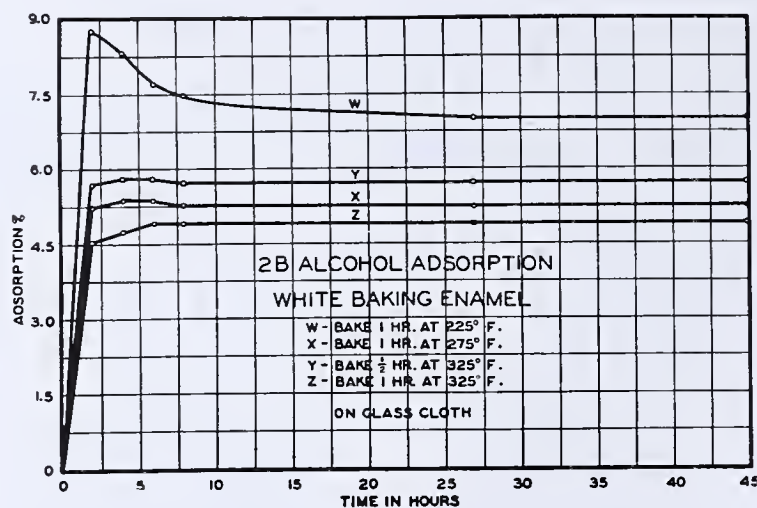


FIGURE 9

These determinations were not made primarily to determine the characteristics of any particular material but to illustrate a method only. For example, a longer baking schedule at 107° C. (225° F.) may have converted the film completely to the insoluble stage and this could have been determined by the method indicated, but that is not the purpose of the present paper.

TABLE VII. VARIATION IN ALCOHOL ADSORPTION WITH BAKING CONDITIONS

Hours	(White baking enamel)					
	Bake 1 Hour at 107° C. (225° F.)			Bake 1 Hour at 135° C. (275° F.)		
	Film 1, 0.6109 g.	Film 2, 0.5801 g.	Av., 0.6005 g.	Film 1, 0.5141 g.	Film 2, 0.5133 g.	Av., 0.5137 g.
	Per cent adsorption					
2	8.81	8.69	8.75	5.06	5.34	5.20
4	8.45	8.21	8.33	5.17	5.50	5.34
6	8.04	7.78	7.91	5.17	5.50	5.34
8	7.60	7.35	7.48	5.09	5.43	5.26
27	7.15	6.89	7.02	5.09	5.36	5.24
45	7.14	6.89	7.02	5.09	5.36	5.24
	Bake 0.5 Hour at 163° C. (325° F.)					
	Film 1, 0.5501 g.	Film 2, 0.5606 g.	Av., 0.5553 g.	Film 1, 0.5147 g.	Film 2, 0.5131 g.	Av., 0.5139 g.
2	5.82	5.55	5.68	4.41	4.66	4.53
4	5.94	5.69	5.81	4.66	4.82	4.74
6	5.94	5.69	5.81	4.86	4.99	4.92
8	5.74	5.44	5.59	4.86	4.99	4.92
27	5.74	5.44	5.59	4.86	4.99	4.92
45	5.74	5.44	5.59	4.86	4.99	4.92

It will be apparent that liquids other than water and alcohol may be used with films on glass cloth to determine permeability, adsorption, and solvent extraction characteristics. The stability of the coated glass cloth would suggest its use in determinations of change of permeability with exterior or accelerated exposure. The coated cloth could be held rigidly in a metal frame which would be noncorrosive, and could be exposed in the same manner as is now customary with coated metal or wooden panels.

### Summary

The value of glass cloth in permeability and adsorption measurements has been shown. The permeabilities of four air-drying materials were compared on Patapar and glass cloth and were found to be in agreement. The glass cloth may be coated on both sides, but the coating may be applied to only one side of the Patapar. The permeabilities of two baking materials were determined satisfactorily on glass cloth. This is not possible on the Patapar because of volume changes due to loss and regain of moisture.

The permeability of a baking material was determined after baking at four different time-temperature schedules, and it was shown that this method may be used to indicate the best baking schedule for maximum resistance.

Water adsorption measurements were made of films on glass cloth and on glass microscope slides and were found to be in agreement. The microscope slide test is standard procedure, but the glass cloth method was shown to have some advantages.

Water adsorption measurements were made of coatings which had been baked on glass cloth at four different time-temperature schedules, and it was shown that the optimum schedule for minimum adsorption may be determined by this method.

Alcohol adsorption was measured on the above baked coatings and the time-temperature bake was determined for maximum alcohol resistance.

Permeability and adsorption measurements were made on test specimens cut from the same piece of coated glass cloth, ensuring uniformity of application and drying conditions on all test specimens.

Evidence has been provided to show the possibilities of glass cloth as a support on which to form films for test purposes. The tests were made with this object in view and no attempt was made to compare the characteristics of the materials used.

### Acknowledgment

The author's appreciation is due the American Cyanamid Company for permission to publish this paper, and for the extensive facilities of the Stamford Research Laboratories.

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# Constructing Apparatus for Electrodialysis

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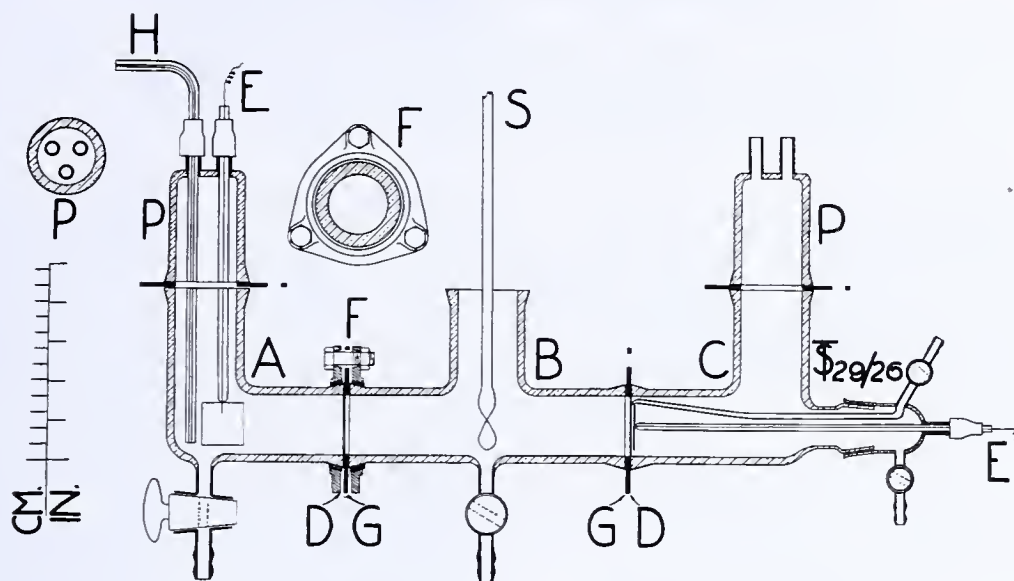


FIGURE 1. TWO TYPES OF THREE-COMPARTMENT CELLS

THE procedure of electrodialysis is of considerable value in many fields of scientific and technological activity. Various types of apparatus for use in electrodialyzing substances have been described from time to time in the literature, and some of these are available commercially through laboratory supply houses. Almost all of these commercial outfits possess one or both of two serious drawbacks. In the first place, many are largely constructed of rubber or some similar material which is entirely unsuitable for use in electrodialytic operations on many substances. Most apparatus which is available is so limited in its flexibility of design that no modifications can readily be made in the size or arrangement of its essential features.

In the course of some work in these laboratories, the authors have had occasion to use procedures involving electrodialysis. In a search for suitable apparatus for their purposes, they have devised a method of constructing electrodialysis cells, which they believe is novel and useful because of its flexibility of design and ease of manipulation.

The important feature of their method of constructing electrodialysis apparatus is the use of stock fittings of Corning industrial flanged Pyrex pipe. These fittings, which are available in a wide variety of shapes and sizes, have been described in considerable detail (1). Figure 1 gives in one composite drawing two types of three-compartment cells which have been built and used by the authors, and serves to illustrate the method of construction.

The middle compartment, B, is a 3.75-cm. (1.5-inch) Pyrex T-fitting to which was sealed a stopcock to act as a drain for the compartment. Simple electrode compartments can be made in the form labeled A from 90° L-fittings of the same size by attaching a stopcock to act as a drain, or a somewhat more elaborate type of electrode compartment can be built as shown by C. This latter design, which is similar to the type of cell devised by Pauli (2), is particularly suitable for removing electrolytes from colloidal substances. Caps, P, for the electrode compartments, were made by drawing down a 15-cm. (6-inch) length of 3.75-cm. (1.5-inch) flanged Pyrex pipe. Three short pieces of 10-mm. Pyrex tubing were sealed to each cap to provide openings for the introduction of electrodes, gas delivery tubes, or funnels, as desired.

The various parts of the apparatus are clamped together by means of the standard metal joint flanges, F, which are supplied for this purpose by the Corning Glass Works. Between the sections, gaskets, G, of various materials may be used to ensure a

tight joint. A very satisfactory gasket can be cut from 0.05-cm. (0.020-inch) thick Eastman acetate sheet. Diaphragms, D, of any suitable membrane material are clamped between the three compartments of the cell in conjunction with the gaskets. The capacity of a cell constructed from 3.75-cm. (1.5-inch) piping is 225 to 275 ml. in the middle compartment, and 125 to 200 ml. in the electrode compartments. The side limb of the center compartment is large enough in diameter to admit a glass stirrer and a Beckman glass electrode and reference half-cell with ease.

The Pauli type of arrangement has been used to remove electrolytes from colloidal silver preparations and to purify hydrophilic colloid preparations, such as starch derivatives.

In addition to its use in colloidal preparations, the equipment is particularly suitable for lecture purposes. An interesting lecture demonstration of the migration of ions in an electric field can be performed with either type of apparatus.

For this purpose, three dyes of different colors and different ionic character were chosen. Such dyes may be, for example, Safranin O (Eastman organic chemical No. 1753), which forms a red cation and a chloride ion; tartrazine (Eastman organic chemical No. P 1163), which dissociates into sodium ions and yellow dye anions; and Chicago Blue-6B (National Aniline Chemical Co., Niagara Sky Blue-6B), which dissociates into sodium ions and blue associated dye anions. If a mixture of these three dyes in solution is electrodialyzed in the above cell fitted with membranes of No. 600 0.0045-cm. (0.0018-inch) Cellophane swelled for 12 hours in distilled water, a clean-cut migration occurs. The safranin goes into the cathode compartment and tartrazine into the anode compartment, with retention of the Chicago Blue in the center compartment. The catholyte is tinted red and the anolyte yellow in from 5 to 20 minutes by applying a potential of 110 volts across the cell. Because of the tendency of the dyes to precipitate one another in certain concentration ratios, care must be taken in making up the mixed solution. This was satisfactorily prepared from the dyes on hand by making stock solutions of safranin containing 0.50 gram per liter, tartrazine containing 2.5 grams per liter, and Chicago Blue containing 0.25 gram per liter. Equal volumes of each were taken and were mixed by adding the safranin to the tartrazine, and then adding the Chicago Blue to the mixture. The electrode compartments contained 0.001 N sodium chloride at the start of the demonstration.

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COMMUNICATION No. 725 from the Kodak Research Laboratories.



# Vacuum Sublimation and Molecular Distillation Apparatus

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TWO kinds of apparatus have proved useful for vacuum distillation of solids in this laboratory.

For relatively large quantities of material, up to 25 grams, the type shown in Figure 1 is eminently satisfactory. Special attention is called to the Pyrex glass cloth, which in practice rests upon the solid being distilled and prevents contamination of sublimate with residue. The cloth can be cleaned with the usual acid cleaning mixture. For molecular distillations the condenser is lowered until it almost touches the cloth.

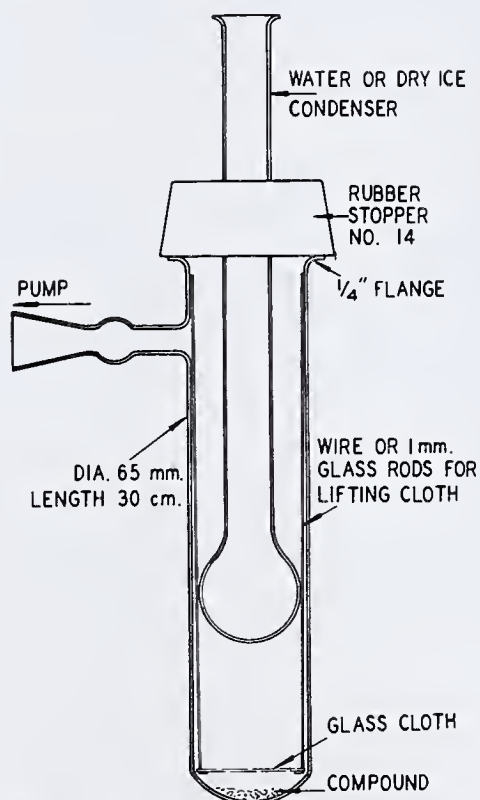


FIGURE 1. VACUUM SUBLIMATION APPARATUS

Large ground joints were used for some time in the apparatus, but, even when carefully lubricated, became jammed together so tightly that breakage and loss of product resulted. The difficulty can be avoided entirely by using the inexpensive nonbreakable connection of rubber stopper and glass flange pictured. The stopper was first cleaned by boiling in alkali, rinsed, dried, and lubricated with stopcock grease. No difficulty was experienced in obtaining a vacuum below 0.2 micron with this connection. Upon releasing the vacuum the joint was easily separated. Similar joints have been used for traps and other connections in vacuum assemblies. Two rubber stoppers can be used in place of the rubber stopper-glass flange arrangement with equal success. It is possible also to rotate the stoppers on each other without destroying the vacuum.

Ordinary stopcock or common lubricating grease has been used as the lubricant, but even more satisfactory is the vaseline residue obtained by distilling the low-boiling components from about 400 ml. of vaseline in a 2-liter flask arranged as a horizontal flask still (2) with air instead of water as the condensing liquid. From about 40 to 65 per cent of low-boiling material is removed before a final temperature of 360° (pressure at 40.50 mm.) is reached in the sand bath used as the heater. Such a lubricant has been mentioned by Burch (1) as admirably suited for work at low pressures. Its freedom from inorganic residues and from low-boiling compounds and its fusion to a clear liquid when warmed make it superior to the common types.

A second apparatus is shown in Figure 2. In this unit the innermost tube containing the sample to be distilled is heated in a jacketed tube, so that the solid is vaporized through the whole length of the tube and collected in a band just beyond the heated portion. A narrow strip of cloth wound around the tube several times and kept cold with water or ice serves as a condenser. A solid carbon dioxide pack or basket may be placed further along the tube to act as an auxiliary condenser or trap. When a fraction is collected at one temperature the heater jacket is moved back about 6 cm., the con-

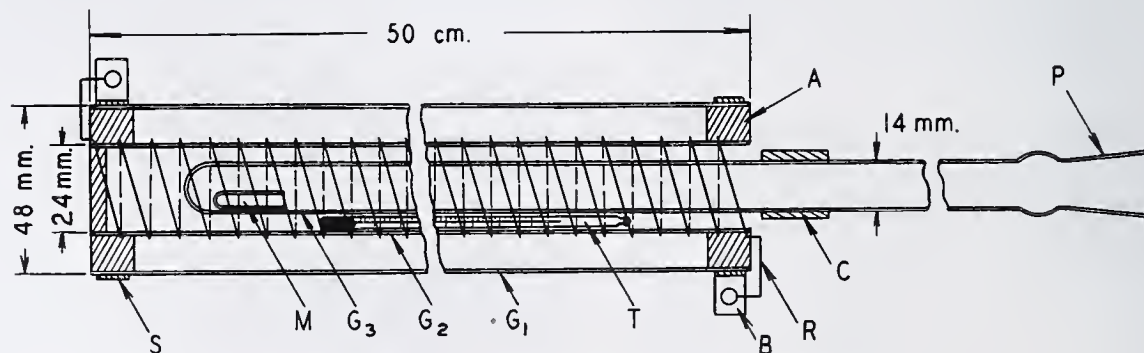


FIGURE 2. FRACTIONAL SUBLIMATION APPARATUS

- A. Asbestos tape
- B. Binding post and fastener
- C. Condenser
- G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub>. Glass tubes 48, 24, and 14 mm. in diameter, respectively
- M. Material being sublimed, contained in glass capsule
- P. Pump connection
- R. Resistance wire
- S. Strip of metal to prevent breakage and serve as support for binding posts
- T. Thermometer



denser moved onto the vacant position, the temperature raised a little, and a new fraction collected. This process is repeated a number of times until a series of bands has been formed. The effect is particularly striking when colored substances are distilled. Apart from its value for distilling small quantities of material, the apparatus is excellent for testing the purity of a compound, since the first and last bands should have identical melting points. It is also good for observing the approximate sublimation temperatures when it is

desired to obtain data preliminary to handling a large batch. Passage of the sublimate through the long tube has little effect on raising the temperature of sublimation if the heating is not too rapid.

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## Electrolytic Assay

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IT IS customary to carry out the electrolytic assay of copper, nickel, and other solutions with the aid of rotating cathodes or anodes, but where their use is inconvenient the electrolyte may be made to rotate instead. This is usually done by placing an electromagnet beneath the electrolyte, thus producing a vertical field, which, in the presence of a current moving radially gives rise to a stirring motion. Several workers have adopted this method of agitating the solution (1-4). When the employment of an electromagnet is impracticable, the same result may be obtained by means of a permanent magnet, within the air gap of which the electrolyte is situated. The following short study is an account of such a magnet and of some results obtained with it.

The magnet was of the four-claw pot type used in loud speakers, but the center pole was truncated and the annular pole enlarged, as depicted in Figure 1. The field produced was substantially vertical at the center pole, becoming almost radial towards the outer one. A pot magnet of the size shown is capable of accommodating beakers of 400-ml. capacity.

The magnet was of 15 per cent cobalt steel, having the following approximate percentage analysis: carbon, 1; cobalt, 15; chromium 9 to 10; molybdenum, 1. The steel was crucible-melted and sand-cast. The casting was sand-blasted, machined, and heat-treated by annealing and hardening. The magnet used for the experiments was devoid of pole pieces; these, when fitted, gave a gap 38 mm. in inside diameter, 41 mm. in outside diameter, and 0.6 cm. (0.25 inch) deep, and an associated flux density of 8500 to 9000 lines, the total flux being 64,000 to 68,000 lines.

Solutions of electrolytic copper were electrolyzed under various conditions of acidity and current density, and for three different times. The volume in each case was 100 ml. The cathode consisted of a circular cylinder of platinum gauze, 2.4 cm. in diameter by 3 cm. high, attached to a central stem by means of cruciform

cross pieces. The anode was arranged to surround the cathode, and was composed of four angle strips attached to a side stem by hoops top and bottom. The cylinder so formed was 4.5 cm. in diameter by 3 cm. high.

Since the stirring effect would clearly be weak at low current densities, experiments under these conditions were not carried out. In the case of mixed acid solutions 1 gram of urea was added to the electrolyte towards the end of the assay. Good, firm deposits were obtained, particularly in the instance of mixed acid solutions.

TABLE I. DEPOSITION OF COPPER

Time Hours	Acidity		Current Amp.	Copper Present Gram	Copper Deposited Gram
	H <sub>2</sub> SO <sub>4</sub> %	HNO <sub>3</sub> %			
0.5	5	..	5	0.4995	0.4783
1.0	5	..	5	0.4995	0.4993
1.5	5	..	5	0.4995	0.4998
0.5	5	..	7.5	0.4995	0.4757
1.0	5	..	7.5	0.4995	0.4993
1.5	5	..	7.5	0.4995	0.4994
0.5	10	..	5	0.4995	0.4696
1.0	10	..	5	0.4995	0.4982
1.5	10	..	5	0.4995	0.4995
0.5	10	..	7.5	0.4995	0.4914
1.0	10	..	7.5	0.4995	0.4993
1.5	10	..	7.5	0.4995	0.4995
0.5	5	5	5	0.4995	0.4814
1.0	5	5	5	0.4995	0.4979
1.5	5	5	5	0.4995	0.4996
0.5	5	5	7.5	0.9990	0.9879
1.0	5	5	7.5	0.9990	0.9954
1.5	5	5	7.5	0.9990	0.9986
0.5	5	5	10	0.9990	0.9940
1.0	5	5	10	0.9990	0.9979
1.5	5	5	10	0.9990	0.9983

The results (Table I) indicate that, although most of the copper is deposited within half an hour, complete removal of the copper from solution does not take place until electrolysis has proceeded for a further hour. At the end of every experiment the electrolyte was tested for copper by means of potassium ferrocyanide; those solutions which had been electrolyzed for the full period (90 minutes) gave a negative reaction. Assays carried out in nitric acid solution yielded poor deposits, and deposition of the metal was incomplete.

The stirring effect of the magnet is appreciable at moderate current densities, and becomes vigorous at high densities. A more powerful magnet than that used in the present study would, of course, enhance the action. Since the magnet is working at a large air gap, it is possible that loss of magnetism may occur in the course of time, although this is unlikely to be serious.

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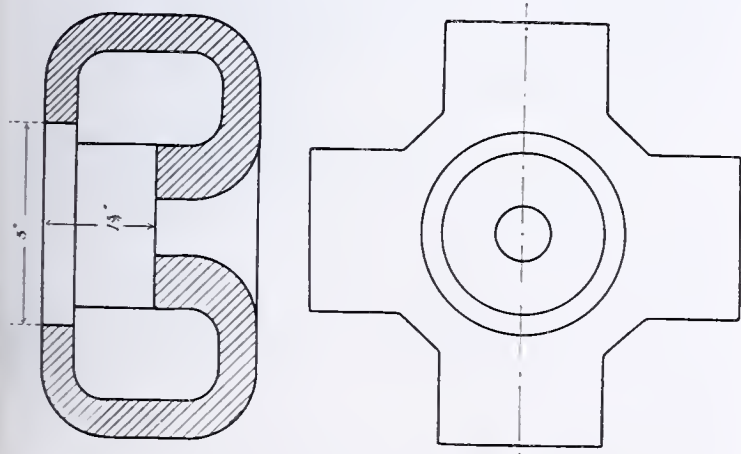


FIGURE 1. PLAN AND SECTIONAL ELEVATION OF MAGNET



## An Improved Thermometer Guard

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A COMMON laboratory problem is the installation of thermometers so that they may be easily removed and at the same time well guarded. In the course of research it was necessary to install ten thermometers on a double-pipe heat interchanger and a guard was developed which is believed to have considerable merit.

The complete guard is shown in Figure 1. The body of the guard, *B*, is a 1-inch length of  $\frac{7}{8}$ -inch hexagonal brass stock, drilled and tapped for a standard  $\frac{3}{8}$ -inch pipe thread. At the bottom of the tapped hole a concentric hole is drilled through of a diameter at least  $\frac{1}{16}$  inch greater than that of the thermometer, *C*, being installed. In addition, three holes are drilled for  $\frac{3}{16}$ -inch welding rods, *D*, which constitute the guards. These rods, of proper length, are threaded or soldered in place and a short piece of  $\frac{1}{8}$ -inch pipe, *E*, is brazed or soldered inside the rods as shown. For the packing, about  $\frac{3}{16}$  inch is cut from the large end of a No. 00 one-hole rubber stopper, so that the remainder, *G*, will not bind in the threads when on the thermometer. Last, a washer, *H*, with  $\frac{9}{16}$ -inch outside diameter

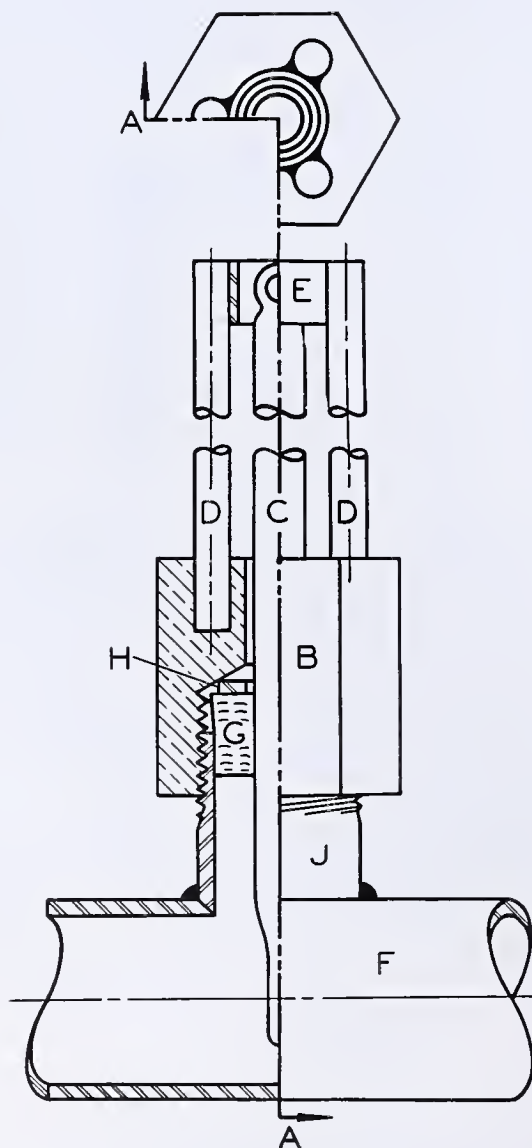


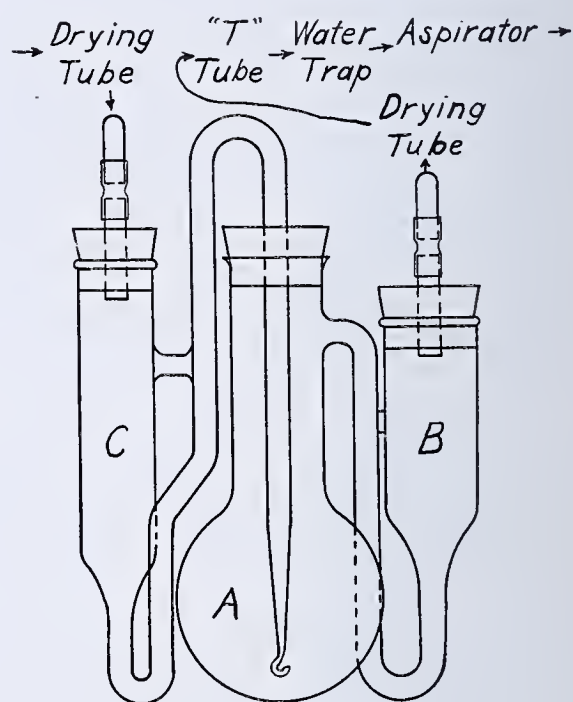
FIGURE 1. DETAILS OF GUARD

and inside diameter the same as drilled in the body, is slipped on the thermometer above the stopper to prevent the stopper's jamming into the body and turning the thermometer as the guard is screwed on.

The assembled guard may be screwed on a  $\frac{3}{8}$ -inch nipple which is in turn screwed into a tee, but a much neater method for permanent installations is shown in the figure. A short length of  $\frac{3}{8}$ -inch pipe, *J*, threaded at one end, is brazed or welded into a hole drilled in the main pipe, *F*, as shown.

## An Alkalimeter

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THE indirect determination of carbon dioxide by means of a simple alkalimeter merits consideration whenever extreme accuracy is not required and speed is of some importance.

Such an alkalimeter of somewhat original design has been used with considerable success in the author's laboratory for the past 3 years. In it are incorporated the advantages attending the use of any of the newer high-efficiency solid desiccants (such as anhydrous calcium sulfate), instead of concentrated sulfuric acid, as well as those arising from the elimination of stopcocks.

*A* is an ordinary 25-cc. distilling flask with a part of the neck cut off. *B* and *C* are ordinary test tubes shortened and drawn down. All pieces should be selected for lightness, since it is desirable that the apparatus weigh as little as possible. Ordinary rubber stoppers are used.

The weighed sample (about 1.5 grams in the case of limestone) is placed in *A*. The desiccant is placed in *B*. Slightly more than enough acid to react completely with the sample is placed in tube *C*. The entire apparatus is assembled, small plugs being placed in the tubes leading from *B* and *C*. The whole piece is then weighed accurately.

Drying tubes containing the same desiccant as that used in the apparatus are attached to *B* and *C*. To the drying tube attached to *B* are connected a T-tube, a water trap, and an aspirator as indicated.



With the aspirator going slowly, the open arm of the T-tube is closed momentarily to start the flow of acid into the reaction chamber, *A*. It is best that the acid be added slowly with some shaking. When all the acid has been added, the open arm of the tube is closed and a slow stream of air is drawn through to remove all the carbon dioxide.

After the apparatus has again reached room temperature, the plugs are attached to *B* and *C* and the apparatus is weighed again. The loss in weight represents the carbon dioxide evolved.

For more detailed general instructions concerning the manipulation, the reader is referred to such texts as Kolthoff and Sandell (*1*).

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## Crucible Support

GILBERT E. SEIL AND H. A. HEILIGMAN, E. J. Lavino and Company, Norristown, Penna.

THE crucible support shown in the drawing offers many advantages to the laboratory in which evaporations, fumings, and ignitions are done in platinum crucibles.

When platinum crucibles are heated on a sand bath or supported in a triangle, many determinations are lost because of the spattering of the residue. Moreover, determinations in adjacent crucibles must be discarded because no near-by crucible is free of suspicion of contamination.

The creep of salts up the sides and over the top of the crucible during the fuming of a residue is a frequent source of annoyance and error. The salts may bake to the outside of the crucible and become contaminated with the sand of the sand bath. Portions of the baked residue may crack and

drop off. A crucible support which eliminates spattering and creep is a valuable adjunct to any laboratory.

The equipment described in this article supports the crucible so that accidental overturning is impossible. The support is easily cleaned and kept clean and, unlike a sand bath, can be moved as required to any convenient location. Filter papers can be quickly and thoroughly dried without charring before ignition.

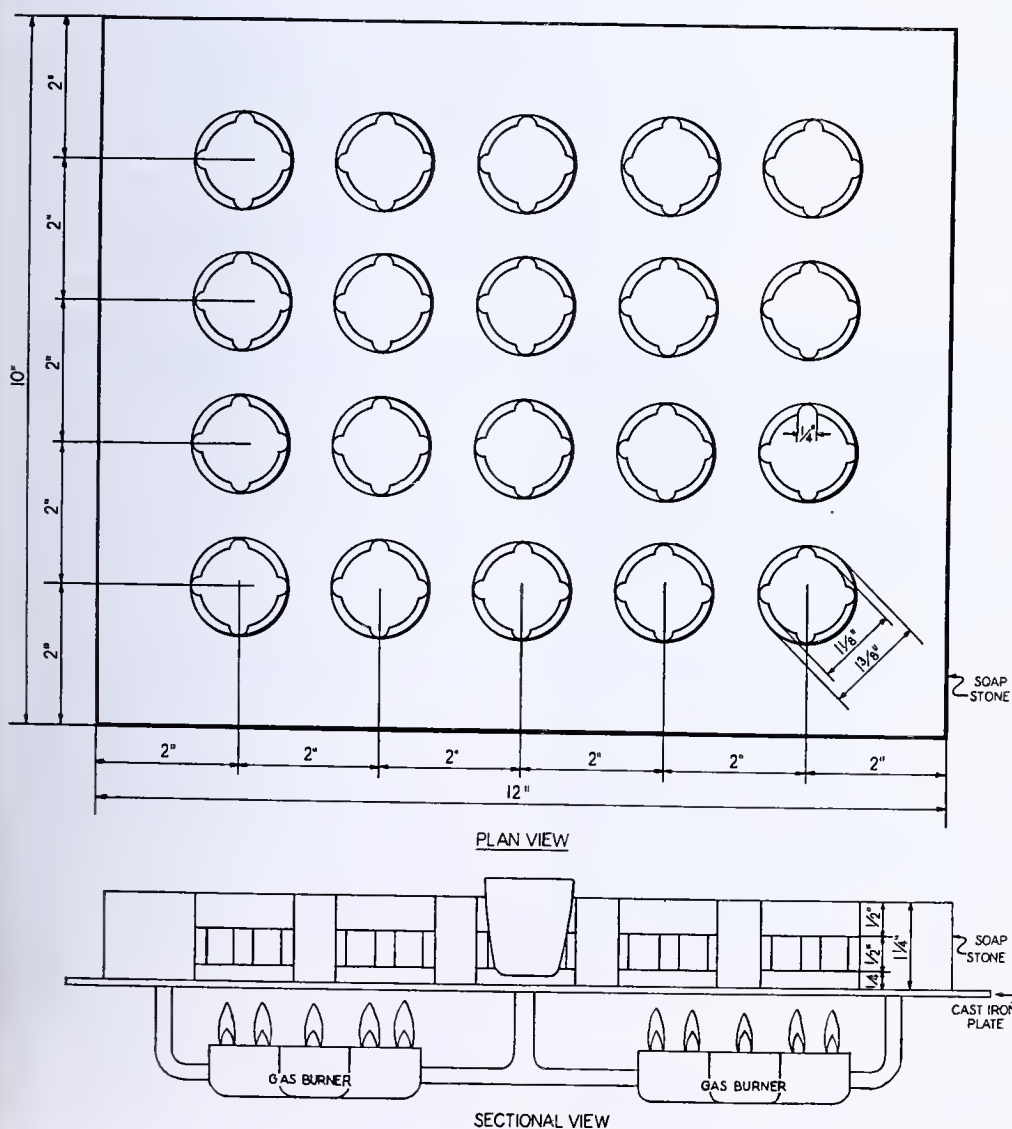
The time required for carrying out a drying, an evaporation, or a fuming in a platinum crucible is reduced by one half as compared with the usual methods. The authors found, for example, that in doing several hundred fluorspar analyses, the time required for volatilizing the silicon tetrafluoride, fuming

the residue with sulfuric acid, and then igniting the calcium sulfate was cut in half by the use of this support. More important, the creep of the salts up the sides and over the top of the crucible was eliminated. No samples were lost because of creep.

The crucible support described is in reality an air bath which distributes the heat around the sides as well as to the bottom of the crucible. It can be conveniently placed on one corner of a hot plate. The authors obtain excellent results with a support placed on an iron plate over a circular gas burner such as is frequently used in kitchen ranges. The size of the support and of the openings can be varied to suit the needs of the individual laboratory.

The authors use several supports in which twenty crucibles (30-ml. capacity) can be treated simultaneously. The supports are easily made from a piece of soapstone  $25 \times 30 \times 3$  cm. ( $10 \times 12 \times 1.25$  inches) drilled as shown in the drawing. First the 0.6-cm. (0.25-inch) holes are drilled at the center of each circle and at the points indicated on the circumference of each circle. Next the 2.8-cm. (1.125-inch) holes are drilled through the stone, and finally the 3.4-cm. (1.375-inch) holes are drilled 1.25 cm. (0.5 inch) from the top of the stone and 0.25 inch from the bottom of the stone.

The crucible will rest in the opening, and the heat will go through the holes along the sides of the crucible, thus heating the sides as well as the bottom. The crucible rests low in the opening and cannot be turned over.





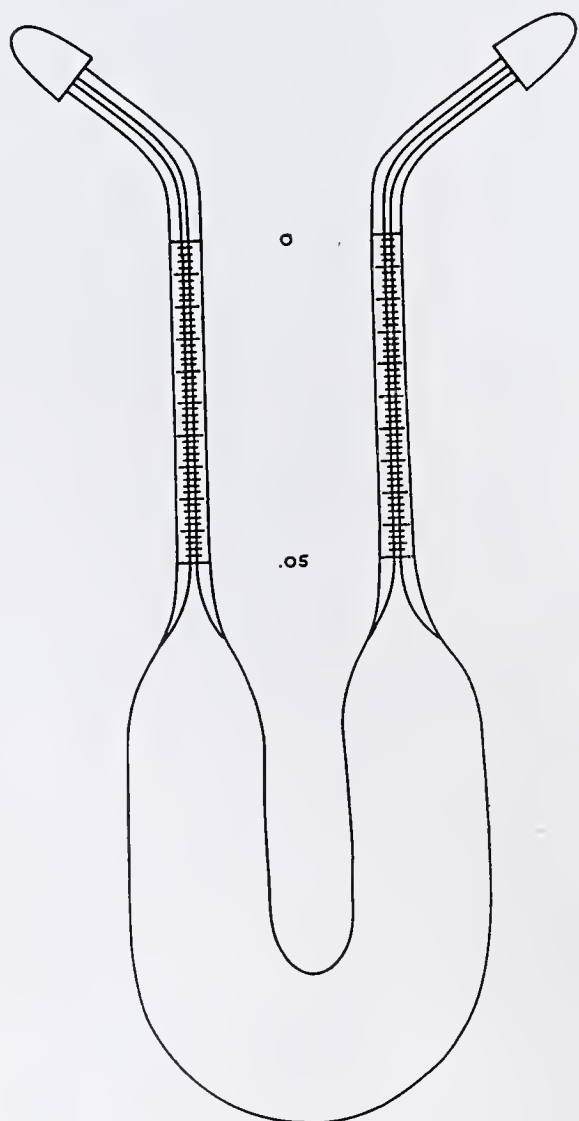
# A Graduated Pycnometer

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University of California at Los Angeles, Calif.

IN AN article concerned primarily with another topic Shedlovsky and Brown (2) incidentally described a new quartz pycnometer featuring two graduated stems. Apparently this item has not been recorded in abstract indexes under "pycnometer" or like caption, and has thus probably escaped deserved attention. The technique of tube graduation needed with the quartz device requires, however, facilities not commonly at hand. The substitution of a standard commercial graduated tube for the quartz tube, as described below, readily permits the construction of a glass pycnometer of the type mentioned. Only ordinary glass-blowing skill is required.

As suggested in the accompanying figure, the upper parts of two graduated pipets are incorporated in a U-tube assembly of 20- to 25-ml. capacity. The current Kimble blue-line Kahn serological pipet, total delivery 0.2 ml., graduated in 0.001-ml. divisions spaced about 1 mm. apart, is used. Probably the most substantial construction is effected by sealing the two segments of pipets to the intervening piece of large tubing first in a straight line. The U-bend is next made, and finally the 45° bends. For workers of limited glass-blowing skill it will probably be easier to prepare the body of the pycnometer in two equal sections connected by a U-tube of small caliper, as illustrated in a commercial Sprengel pycnometer now on the market (1). Such a modification is not quite so easily filled, however.



Economy may be attained by sacrificing only one pipet, from which two graduated sections are cut. The resulting irregularity in numerical markings detracts from the appearance of the finished pycnometer, but not from its usefulness. The 45° angles at the top facilitate drainage, in contrast to certain older Sprengel-type pycnometers, but make filling more difficult where a rubber connecting tube is not permissible. In the latter case a ground-on glass angle tube may be prepared to fit in place of one of the glass caps.

The pycnometer is suspended in a thermostat with side window or equivalent, and is read with complete immersion of the filled portion. In calibration it is filled with the usual air-free distilled water approximately to mid-positions on the graduated stems. The true volume, presumably at 20° or 25° C., is then calculated for the contents represented by the two stem readings. It makes no difference whether these stem readings are at the same horizontal level. In 1-mm. capillary tubes very slight irregularities cause decided differences in position of meniscus.

When the pycnometer is ready to receive the liquid under investigation, it is not necessary to fill to the same marks recorded for water. Even should the level on each side be as far as 0.010 ml., or 10 scale divisions, from the position of calibration, and the temperature of the thermostat be 5° from the standard 20° at which the pipet was graduated, the error is negligible.

It is convenient to post a reference value for the volume of the pycnometer filled on both sides to the zero marks. In each subsequent determination one need only subtract the sum of the two new scale readings from the posted constant.

**CALIBRATION.** Pycnometer holds 20.4692 ml. at readings 0.0245 and 0.0270 (sum 0.0515). Posted reference value is  $20.4692 + 0.0515 = 20.5207$  ml.

**DETERMINATION.** Pycnometer is filled to readings 0.0305 and 0.0322 (sum 0.0627). Volume of contents is  $20.5207 - 0.0627 = 20.4580$  ml.

If the pycnometer carries one stem with larger numbers, as in the "economy" model described, no new trouble is encountered. A posted reference value for zero reading may still be computed exactly as in the example given above. Such zero reading has only arithmetical significance, however, since it is physically impossible to fill the device to zero on both sides.

If this pycnometer should be produced by a manufacturer, who obviously does his own tube graduation, the two zero marks should be at the lower ends, with scales reversed. This change makes the arithmetic involved in density determination more straightforward and more quickly understood. The device may then be likened to a precision graduated cylinder to be calibrated for contents. Since the scales are read while the pycnometer is immersed in a thermostatic bath, the blue-line feature is especially desirable.

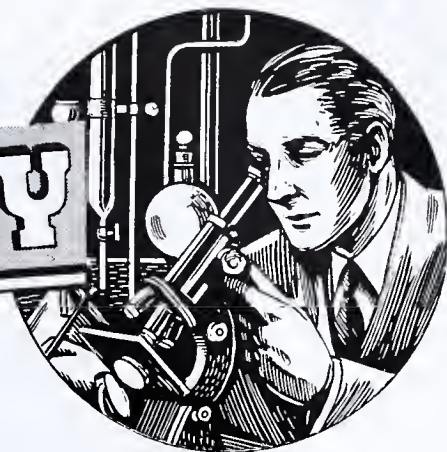
This pycnometer has the conveniences of flushing and filling long known in the Sprengel models. Furthermore the new device shows directly and continuously, without call for adjustment of any kind, when the contained liquid is at the constant temperature of the bath. The inaccuracy involved in bringing a meniscus to a mark, as in models requiring application of filter paper, is not involved. Since there is no fitting of a tapered ground stopper, the errors due to uncertainty of seating of such joints are not present.

## Literature Cited

- (1) Central Scientific Co., Chicago, Ill., Catalog item 15,775.
- (2) Shedlovsky, T., and Brown, A. S., *J. Am. Chem. Soc.*, **56**, 1066 (1934).



# MICROCHEMISTRY



## Estimation of Anthraquinone-1,8-Disulfonic Acid

### Microscopic Method for Use in the Presence of Certain Other Anthraquinone Sulfonic Acids and Sulfuric Acid

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WHEN anthraquinone is sulfonated in the presence of mercury in order to form the disulfonic acids, a mixture is formed which is composed mainly of 1,5-disulfonic acid and 1,8-disulfonic acid with some 1,6- and 1,7-acids. A method was needed for the identification and estimation of the 1,8-acid in a mixture of the 1,8-acid, the 1,5-acid, and sulfuric acid, from which the 1,6-acid and the 1,7-acid had already been removed.

A method which has been used for a similar purpose (3) involves as one step the conversion of the disulfonic acids to the corresponding dichloroanthraquinones by the action of sodium chlorate and hydrochloric acid, and as another step the hydrolysis of  $\alpha$ -sulfonic groups (in order to determine the presence of  $\alpha$ - and  $\alpha,\beta$ -sulfonic acids). Another method (1, 4, 6) also involves the preparation of the mixed dichloroanthraquinones, whose melting point is taken. The con-

centration of 1,8-acid is determined from a mixed melting point diagram for 1,5- and 1,8-acids. These methods are time-consuming. Furthermore, the melting point would be depressed by impurities other than the 1,8-dichloroanthraquinone; consequently a high value for 1,8-acid would be obtained.

The method which is reported here is based on a new principle. When a mixture of sulfuric acid, anthraquinone-1,5-disulfonic acid, and anthraquinone-1,8-disulfonic acid is treated under standardized conditions with barium chloride, the barium salt of the 1,8-acid is precipitated in such a form that it may be distinguished from the barium salts of the other two compounds by microscopic examination. It forms anisotropic, prismatic crystals, which exhibit parallel extinction, whereas the other two barium salts form aggregates which appear to be amorphous under ordinary magnifications.

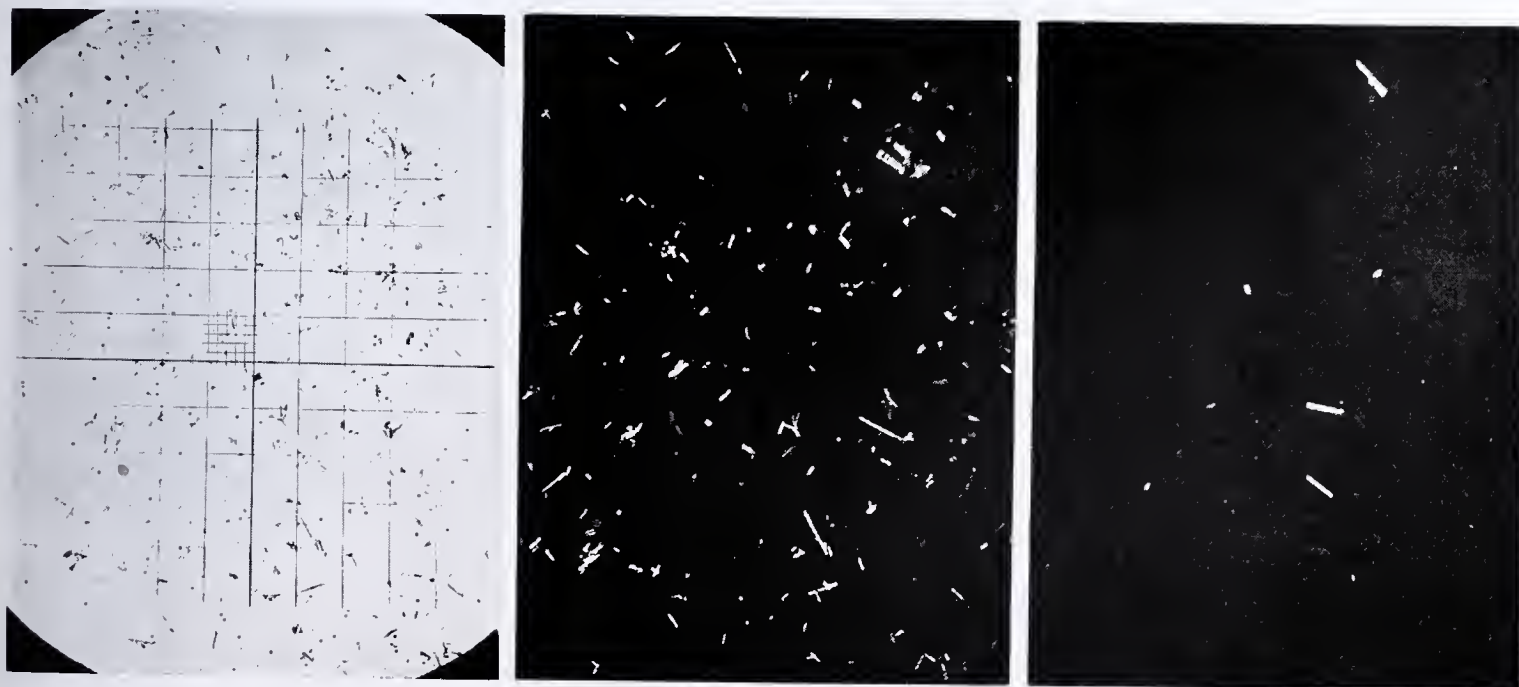


FIGURE 1. PHOTOMICROGRAPHS OF BARIUM SALTS OF 1,5-, 1,8-, AND SULFURIC ACIDS  
A. 18 per cent 1,8-acid; 62 per cent 1,5-acid; 20 per cent sulfuric acid. Bright-field illumination.  
B. Same slide as A between crossed Nicol prisms.  
C. 4 per cent 1,8-acid; 76 per cent 1,5-acid; 20 per cent sulfuric acid. Between crossed Nicol prisms.



When the mixture of barium salts is examined between crossed Nicol prisms, under suitable conditions of illumination, the 1,8-salt appears as brilliantly glistening specks or prisms (depending upon the size of the crystals) which can be readily distinguished from the black or grayish aggregates of the other two barium salts (Figure 1). By means of a systematic method of counting, it is possible to get a quantitative relationship between the number of crystals of the 1,8-barium salt and the percentage of 1,8-acid in the original mixture.

It is inevitable, of course, when a precipitation is made, that the precipitated crystals will differ in size among themselves, and so it might seem impossible to get consistent values in relation to the concentration of 1,8-acid without some system of weighting the counted crystals. Actually this is not necessary, because when the precipitation is carried out under standardized conditions, the small and the large crystals seem to be formed in some constant proportions, so that it is possible by counting all crystals alike regardless of size to obtain a linear relationship between the count and the percentage of 1,8-acid, within certain limits of concentration of the latter (Figure 2).

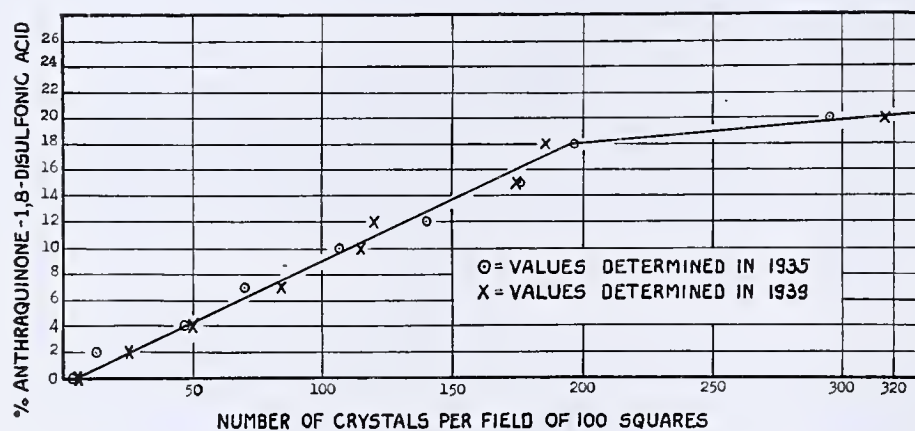


FIGURE 2. RELATIONSHIP BETWEEN COUNT AND PERCENTAGE OF 1,8-ACID

The method was worked out in detail for mixtures containing 20 per cent of sulfuric acid and 80 per cent of variously proportioned 1,5- and 1,8-acids. The latter varied between 0 and 20 per cent. For such mixtures it was found that the 1,8-acid could be estimated with a probable error for a single determination of  $\pm 0.5$  per cent (absolute) of 1,8-acid. This error represents both precision and accuracy. Of course, more accurate values can be obtained by averaging more than one value. In this case the probable error of the mean would be  $\pm 0.5\% / \sqrt{n}$ , where  $n$  is the number of values averaged.

This work was aimed primarily at a method for distinguishing 1,8-acid from 1,5-acid, but incidentally three other sulfonic acids were tried: the 2,6- and 2,7-disulfonic acids and the 2-monosulfonic acid. (The 1,6- and 1,7-disulfonic acids and the 1-monosulfonic acid were not available.) It was found that the 2,7- and the 2-acids behaved like the 1,5-acid and sulfuric acid, when they were in the presence of the 1,5-acid and sulfuric acid alone; but in the presence of the 1,8-acid too, they seemed to lower the values which were found for the 1,8-acid.

Not enough work has been done with these mixtures to enable the author to draw definite conclusions concerning the likelihood of perfecting a method to eliminate these interferences. The 2,6-acid interferes, since its barium salt forms anisotropic needles under the conditions of the method, which are counted with the crystals of the barium salt of the 1,8-acid. The effect of the 2,6-acid was only of incidental interest, and too few experiments were made with it to permit drawing many conclusions, but it would seem possible to

devise a technique for estimating the total percentage of 1,8- and 2,6-acids when they are present together with the 1,5-acid and sulfuric acid. It should also be possible to estimate the percentage of the 2,6-acid in the absence of the 1,8-acid but in the presence of the 2,7-acid or the 2-acid, or both (Table II). Since conditions of sulfonation which lead to the production of 1,8-acid do not lead to the production of 2,6-acid (3, p. 220), these two would not normally interfere with each other.

It is reported that the barium salt of the 1-sulfonic acid crystallizes in needles (5). Since the author has found that the 2-acid precipitates in a form similar to the 1,5- and 2,7-acids, it may be possible to develop a method for the estimation of the 1-acid in the presence of the 2-acid, based on the principle described here.

## Procedure

A curve is first constructed which is based on the precipitation of the barium salts of a mixture of such acids as would be present in the samples which are to be analyzed.

**CHEMICALS.** *Barium Chloride.* The ordinary reagent grade of barium chloride dihydrate was used.

*Anthraquinone-1,8-disulfonic Acid.* The crystals of the 1,8-acid, which had separated from a sulfuric acid wash liquor obtained in the preparation of the 1,5-acid, were precipitated from aqueous solution by means of concentrated hydrochloric acid. The precipitate was recrystallized three times from a mixture of 19 parts by weight of acetic acid and one part of water, with the addition of decolorizing carbon. The product, after drying for 2 hours in a steam oven and then in a vacuum desiccator, melted at  $299.5\text{--}300.5^\circ\text{C}$ . (cor.) with decomposition. An additional recrystallization from 19 to 1 acetic acid did not change the melting point. Titration with 0.1 *N* sodium hydroxide (methyl red indicator) gave a value of 82.7 per cent of  $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2$  or 102.9 per cent of  $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2 \cdot 5\text{H}_2\text{O}$ . The drying at steam-oven temperature had partially dehydrated the pentahydrate.

*Barium Salt of 1,8-Acid.* An aqueous solution of the 1,8-acid was precipitated with a solution of barium chloride. The barium salt was filtered and washed with water.

*Anthraquinone-1,5-disulfonic Acid.* An alcoholic solution of the crude 1,5-acid was treated with an alcoholic solution of monomethylaniline. The precipitated monomethylaniline salt of the 1,5-acid was washed with alcohol and recrystallized from a mixture of 4 parts by volume of alcohol and 5 parts by volume of water. This product, as well as a small portion which was recrystallized again from the 4 to 5 alcohol, melted with decomposition at  $252.5\text{--}253^\circ\text{C}$ . (cor.) when the melting point tube was immersed in a bath previously heated to  $240^\circ\text{C}$ . The monomethylaniline salt was warmed gently with a slight excess of dilute sodium hydroxide solution, and the liberated monomethylaniline was steam-distilled.

The 1,5-acid was precipitated from the solution of its sodium salt in the form of the barium salt, and this was decomposed with sulfuric acid. After removing the precipitated barium sulfate, the solution of the 1,5-acid was concentrated and then treated with hydrochloric acid to precipitate the free 1,5-acid. This was recrystallized from 19 to 1 acetic acid and dried in the steam oven. The product, as well as a small portion which was recrystallized once more from acetic acid (19 to 1), melted with decomposition at about  $313^\circ\text{C}$ . (cor.). Titrations with 0.1 *N* sodium hydroxide (methyl red indicator) gave a value of 84.0 per cent of  $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2$  or 100.4 per cent of  $\text{C}_{14}\text{H}_6\text{O}_2(\text{SO}_3\text{H})_2 \cdot 4\text{H}_2\text{O}$ .

*Anthraquinone-2,6-disodium Disulfonate.* The ethylbenzyl-aniline [ $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)\text{CH}_2\text{C}_6\text{H}_5$ ] salt of the 2,6-acid was prepared by treating a hot aqueous solution of the crude 2,6-acid with a dilute hydrochloric acid solution of ethylbenzylaniline. The salt was recrystallized from methyl and ethyl alcohols (1 to 1 by volume) three times. The melting point [ $238.4\text{--}238.7^\circ\text{C}$ . (cor.)] did not change upon recrystallization from butyl alcohol. The purified salt was hydrolyzed with sodium hydroxide solution and the last trace of ethylbenzylaniline was removed by steam distillation. The disodium salt of the 2,6-acid was recovered by concentrating the residual solution which was left after steam distillation. It was then recrystallized from water.



Analysis. Sodium (calculated from the sulfated ash), 11.04, 11.16; average, 11.10 per cent. Sulfur, 15.55, 15.55 per cent. Calculated for  $C_{14}H_6O_2(SO_3Na)_2$ : sodium, 11.16 per cent; sulfur, 15.55 per cent.

**Anthraquinone-2,7-disodium Disulfonate.** The ethylbenzyl-aniline salt was prepared in a manner similar to that described for the 2,6-acid. It was recrystallized twice from a solvent made up of one part by volume of alcohol and 3 parts of water. The melting point [149.8–151.2° C. (cor.)] did not change upon an additional recrystallization from butyl alcohol.

Analysis. Micro Dumas nitrogen, 3.45 per cent; calculated for  $C_{14}H_6O_2(SO_3H)_2(C_6H_5N.C_2H_5.CH_2C_6H_5)_2$ , 3.54 per cent.

The salt was treated with sodium hydroxide solution in order to liberate the ethylbenzylaniline. The last traces of the latter were removed by extraction with ether, the solution was concentrated, and the 2,7-disodium disulfonate was thrown out by the addition of alcohol. It was redissolved, then reprecipitated by means of alcohol, and dried at 110° C.

Analysis. Sodium (calculated from the sulfated ash), 11.08, 11.18; average, 11.13 per cent. Sulfur, 15.64, 15.49; average, 15.57 per cent. Calculated for  $C_{14}H_6O_2(SO_3Na)_2$ : sodium, 11.16 per cent; sulfur, 15.55 per cent.

**Anthraquinone-2-sodium Sulfonate (Silver Salt).** The crude anthraquinone-2-sodium sulfonate was precipitated as the monomethylaniline salt by treating its hot solution with an aqueous hydrochloric acid solution of monomethylaniline and cooling. The methylaniline salt was recrystallized from dilute alcohol, and a portion of these crystals was recrystallized from benzene. Both products melted at 201.2–202.0° C. (cor.) with slight decomposition, when the melting point was taken in a bath previously heated to 185° C.

The methylaniline salt was hydrolyzed by means of sodium hydroxide solution and the anthraquinone-2-sodium sulfonate was recrystallized from water.

Analysis. Sodium (calculated from sulfated ash), 7.41, 7.41 per cent; calculated for  $C_{14}H_7O_2.SO_3Na$ , 7.41 per cent.

**REAGENT SOLUTIONS.** A. Saturate distilled water with the barium salt of 1,8-acid at room temperature and filter. The solution should be perfectly clear. The solubility of the barium salt is reported as 1 part in 3600 parts of water at 18° C. and 100° C. (2), yet even this slight solubility would interfere sufficiently with the complete precipitation of the barium salt of the 1,8-acid, so that it is necessary to use A for all solutions which are to be used in the method.

B. Dilute 0.590 gram of barium chloride dihydrate with A to 100 ml., with the addition of a little barium salt of 1,8-acid. Shake well and allow whatever barium salt will precipitate from A, because of the common-ion effect of the barium chloride, to do so over a period of several hours. Filter and use the clear solution.

C. Make up 0.0125 gram of anthraquinone-1,8-disulfonic acid to 100 ml. with A. This solution contains 0.1 mg. of anhydrous 1,8-acid per ml.

D. Make up 0.1190 gram of anthraquinone-1,5-disulfonic acid to 100 ml. with A. This solution contains 1.0 mg. of anhydrous 1,5-acid per ml.

E. Make up 0.0112 gram of anthraquinone-2,6-disodium disulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2,6-acid per ml.

F. Make up 0.0112 gram of anthraquinone-2,7-disodium disulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2,7-acid per ml.

G. Make up 0.0108 gram of anthraquinone-2-sodium sulfonate to 100 ml. with A. This solution contains, as the sodium salt, the equivalent of 0.1 mg. of anhydrous 2-acid per ml.

H. 0.1 N sulfuric acid; 0.4 ml. is equivalent to 2 mg. of sulfuric acid.

**STANDARD SOLUTIONS.** Make up mixtures of the reagent solution so that each solution will contain a total of 10 mg., distributed between the sulfuric acid and the various sulfonic acids. In all this work each solution had 0.4 ml. of 0.1 N sulfuric acid (2 mg. of sulfuric acid) plus 8 mg. of total sulfonic acids. Each milligram of sulfonic acid is equivalent to 10 per cent of the total sulfuric acid plus sulfonic acids. Add sufficient A so that the total volume of the solution will be 30 ml.

**PRECIPITATION OF BARIUM SALTS.** Place 10 ml. of B in a 50-ml. beaker provided with a small stirring rod. Place the 30 ml. of standard solution in a buret or pipet and, with continuous vigorous stirring, add it to B drop by drop, very slowly at first, and somewhat faster as the solution becomes turbid, in such a manner that it takes about 4 to 5 minutes to add the entire 30 ml. Continue stirring vigorously for 10 minutes, scratching the sides of the beaker at the same time. Allow the beaker to stand overnight, stirring occasionally, before taking a sample for a crystal count.

**PREPARATION OF CELL AND COUNTING OF CRYSTALS.** Prepare a counting cell by cementing a flat ring upon a microscope slide. The cell which was used in this work was 9.5 mm. in diameter and 0.29 mm. in depth. Cells of any other practical dimensions may be used, provided that the curve is based upon the use of the same cell as will be used for the analysis.

Agitate thoroughly with a stirring rod the beaker which contains the precipitated crystals, and remove a drop of the mixed liquid on the end of the rod. Touch the drop to the center of the cell. Remove another drop, after thorough agitation, and touch this to the first drop. Immediately place a cover glass upon the cell, pressing it down as soon as it is in position, in order to squeeze out excess liquid before the crystals in the excess have had much time to settle. Allow the cell to stand for 2 minutes before examining.

Examine the cell between crossed Nicol prisms with a visual magnification of X70. In this work there was used a Leitz X10 objective, a tube length of 170 mm., and a X7 micrometer ocular with a Whipple disk. Under these conditions of magnification, a side of each of the 100 small squares corresponded to a length of 0.124 mm. as measured by comparison with a stage micrometer.

First focus the microscope upon the crystals with the analyzer removed. Then insert the analyzer in the crossed position with respect to the polarizer. Adjust the illumination so as to bring the crystals of the 1,8-barium salt into the greatest prominence and lower the condenser sufficiently so that the aggregates of barium sulfate and of the 1,5-barium salt will appear as dull, grayish particles. If the condenser is raised too high, these barium salts will appear bright and confuse the counting of the 1,8-barium salt crystals.

Count the 1,8-barium salt crystals systematically in each field of 100 squares. Count as one crystal every particle in each small square which appears brilliantly illuminated, regardless of its size. Some particles will appear merely as barely perceptible bright specks and others may extend across several small squares. There will be some well-formed prismatic crystals which happen to be lying in the positions of extinction and so, although not illuminated, are nevertheless perceptible and obviously different from the background of barium sulfate and 1,5-barium salt. Count these together with the illuminated crystals. In counting, count one small square at a time, and count as one crystal every crystal in a small square and any part of a crystal which crosses a line into a small square. In this way many crystals are counted more than once, but this partially compensates for the variations in the sizes of the individual crystals.

Sometimes, for samples with a high crystal count, some crystals remain out of focus when the count is taken by focusing upon the crystals at the surface of the slide. By focusing up, these crystals are brought into view, and should be included in the count for a given field. It has been found necessary to focus twice in this way only occasionally, and then only for fields with high counts. Record the total count for 100 small squares. Examine six fields on each slide, changing the position of the slide without looking at the field through the microscope, so as to avoid being influenced in placing the slide by the number of crystals in a field. Calculate the average number of crystals per field and plot the number of crystals against the percentage of 1,8-disulfonic acid (Figure 2).

Up to a crystal count of 200 the per cent of 1,8-acid can be calculated by the following equation, which fits the curve:

$$\% \text{ of 1,8-acid} = \frac{\text{number of crystals}}{11}$$

**ANALYSIS OF SAMPLES.** Weigh 0.100 gram of the sample, which contains sulfuric acid and the 1,5- and 1,8-disulfonic acids. Make up to 50 ml. with A. Pipet a 5-ml. aliquot and dilute with 25 ml. of A. Then treat as described for the standard solutions. Read the value of 1,8-acid from the curve or calculate by means of the equation.

**RATE OF PRECIPITATION.** It is necessary to standardize the method of precipitation of the barium salts; otherwise the crystal count may not be reproducible. Some experiments were made in which the solution of the acids was added to the barium chloride solution directly from a 50-cc. beaker over a period of about 5 minutes. The difference in this method from that described in the procedure lay mainly in the fact that the additions of the solution were in quantities more than a drop at a time. This procedure resulted in counts which for two mixtures were lower than those for normal precipitations, whereas with one mixture the count was normal. Table I gives the values obtained. The reason



TABLE I. EFFECT OF METHOD OF PRECIPITATION UPON CRYSTAL COUNT

Method of Precipitation	1,8-Acid %	Crystal Count
Normal	5	58
Abnormal	5	51
Normal	12	134
Abnormal	12	75
Abnormal	12 <sup>a</sup>	97

<sup>a</sup> This sample had 5 per cent of 2,6-acid in addition to the 1,8-acid and should consequently have had an even higher count than that which was normal for 12 per cent of 1,8-acid.

for this behavior may possibly lie in the fact that, when the solution is added too rapidly, the relatively lower concentration of barium chloride which meets the sulfonic acids, as compared with that in the slower addition, results in the formation of fewer nuclei and consequently larger crystals.

have had some influence upon the results, since the curve was based upon material which contained no sodium salts.

### Precision and Accuracy

In counting crystals, it was found that if six fields from one slide are counted, the values for the individual fields may vary considerably, yet the average count for the six fields will agree well with the average for six fields from another slide prepared from the same mixture. Table III illustrates the agreement which may be expected.

From the slope of the curve (Figure 2) between the range of 0 to 200 crystals, it can be calculated that, within that range about 11 crystals are equivalent to 1 per cent of 1,8-acid; between about 200 to 300 crystals the ratio is about 50 crystals for 1 per cent of 1,8-acid. The mean crystal count for two slides differs from the count for each slide by a value which is equivalent to less than  $\pm 1$  per cent of 1,8-acid (absolute).

TABLE II. EFFECT OF SULFONIC ACIDS OTHER THAN 1,5- AND 1,8-ACIDS

[All solutions contained 0.4 ml. of 0.1 N H<sub>2</sub>SO<sub>4</sub> (2 mg. of H<sub>2</sub>SO<sub>4</sub>)]

Solution	1,5-Acid Mg.	1,8-Acid Mg.	2,6-Acid Mg.	2,7-Acid Mg.	2-Acid Mg.	1,5-Acid %	1,8-Acid %	2,6-Acid %	2,7-Acid %	2-Acid %	Crystal Count	Crystal Count Calculated as % 1,8-Acid
XVII	6	0	2	0	0	60	0	20	0	0	Many fine needle crystals. Slide not counted	
XVIII	6	1	1	0	0	60	10	10	0	0	228	18
XIX <sup>a</sup>	4	0.5	1.5	0	0	50	6.25	18.75	0	0	221	18
XX <sup>a</sup>	7	1.5	0.5	0	0	63.6	13.6	4.55	0	0	104, 83	8
											Av. 94	
XX' <sup>b</sup>	6	1.5	0.5	0	0	60	15	5	0	0	177	16
XXI	6	0	0	2	0	60	0	0	20	0	None	0
XXII	6	0	0	0	2	60	0	0	0	20	None	0
XXIII	6	1	0	0.5	0.5	60	10	0	5	5	22	2
XXIV	6	0.5	0	0.8	0.7	60	5	0	8	7	24	2

<sup>a</sup> Contained a total of sulfonic acids and sulfuric acid which differed from the normal 10 mg.

<sup>b</sup> This sample inadvertently did not have sulfuric acid added at start of precipitation; it was added after about half of solution had been added to barium chloride solution.

Evidence that reproducibility does not depend upon an unconscious duplication of a technique which is not susceptible of adequate description is offered by the fact that the curve in Figure 2 represents determinations made four years apart; no determinations were made in the intervening period.

TIME OF STANDING BEFORE COUNTING. Frequently a preparation will attain its maximum count if it is allowed to stand with occasional stirring for 2 hours after precipitation. Sometimes, however, the count after 2 hours will be low. If the mixture is allowed to stand overnight, the count will always have attained a maximum value which is constant, since an additional period of one day causes no increase.

INTERFERING SUBSTANCES. Table II indicates the results of some experiments which were made to test the effect of acids other than the 1,8- and 1,5-acids in the method. These acids were added in the form of the sodium salts, but the percentages were calculated on the basis of the free acids.

Several conclusions may be drawn. The 2,6-acid interferes with the estimation of 1,8-acid, since it precipitates as anisotropic needles in the absence of the 1,8-acid (XVII). Experiments XVIII, XIX, XX, and XX' indicate that the values for 1,8- and 2,6- are not additive under the conditions of the estimation of 1,8-acid, but it may be possible to devise conditions such that the two would be additive. One such condition would, of course, be to use as diluent water which has been saturated with the barium salt of both the 2,6-acid and the 1,8-acid. It appears that, although when the 2,7-acid and the 2-acid are each present separately with the 1,5-acid and without the 1,8-acid, they deposit no crystals which can be counted, yet when they are both present together with the 1,8-acid, they lower the count of 1,8-acid. The use of the sodium salts of the 2,6-, 2,7-, and 2-acids may

The points which are plotted on the curve represent separate determinations. One set of points was made four years after the other set. The mean deviation of these points from the curve in terms of per cent of 1,8-acid is  $\pm 0.5$  per cent (absolute) for 18 values. The probable error for a single value may also be calculated as  $\pm 0.5$  per cent of 1,8-acid (absolute). This represents both the precision of the method and the deviation from the true value of 1,8-acid. The method does not involve any constant error. If more than one determination is made, the mean value will have a probable error of  $\pm 0.5/\sqrt{n}$  per cent, where  $n$  equals the number of values averaged to get the mean value.

TABLE III. CRYSTAL COUNTS IN INDIVIDUAL FIELDS AND AVERAGES

Solution A		Solution B		Solution C	
Slide 1	Slide 2	Slide 1	Slide 2	Slide 1	Slide 2
36	34	163	153	279	292
48	32	163	171	272	315
41	37	158	112	256	298
40	34	164	141	266	268
34	40	164	148	311	296
43	34	177	162	292	261
Av. 40	35	165	148	279	288
Grand av. 38		157		284	

### Summary

A method has been devised for the estimation of anthraquinone-1,8-disulfonic acid in admixture with sulfuric acid and anthraquinone-1,5-disulfonic acid which involves precipitating the barium salts of the three acids and counting



the crystals of the barium salt of the 1,8-acid under the microscope between crossed Nicol prisms. The method was investigated for mixtures containing 20 per cent of sulfuric acid, 0 to 20 per cent of 1,8-acid, and 60 to 80 per cent of 1,5-acid. The probable error of a single value is  $\pm 0.5$  per cent of 1,8-acid (absolute). The method involves no constant error.

Anthraquinone-2,6-disulfonic acid interferes and is estimated together with the 1,8-acid. The method might be developed for mixtures containing 2,6-acid in the presence or absence of 1,8-acid. Anthraquinone-2,7-disulfonic acid and anthraquinone-2-sulfonic acid may cause low values for the 1,8-acid. It might also be possible to develop a method for the estimation of anthraquinone-1-sulfonic acid in the presence of anthraquinone-2-sulfonic acid, based upon the principle described.

### Acknowledgments

Acknowledgment is made of the cooperation of A. R. Norton in furthering the study of the method; of the assistance of G. L. Royer in preparing the photomicrographs; and of the assistance of W. J. Mader in preparing the sodium salts of anthraquinone-2,6-, -2,7-, and -2-sulfonic acids.

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## A Distillation Capillary

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MIXTURES of low boiling liquids, in volumes as small as 0.02 to 0.1 ml., can be fractionally distilled by means of the apparatus described below.

### Preparation of Distillation Capillary

A piece of Pyrex glass tubing, *A*, about 8 mm. in outside diameter, and with 1-mm. wall, is heated in the blast lamp and drawn out to a capillary, *B*, somewhat longer than 10 cm., with a uniform inner bore of approximately 2 mm. A 10-cm. section, *C*, of this capillary is cut off. About 5 cm. from one end, the capillary is drawn out to a much finer capillary, *D*, 0.25 to 0.5 mm. in outside diameter, and about 7 cm. long. Any excess length is cut off. The end of the finer capillary is sealed by heating in the flame.

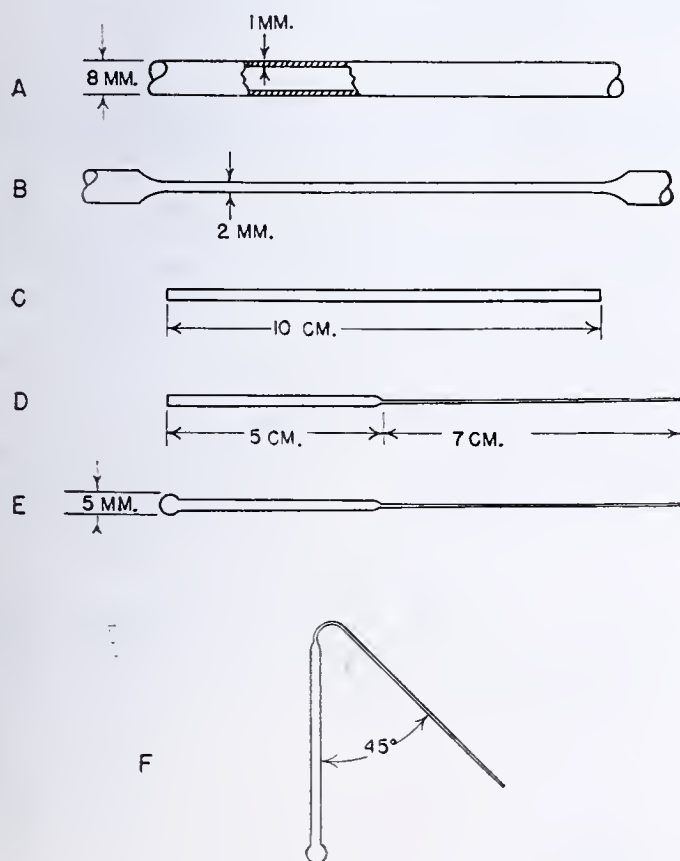


FIGURE 1

The end of the larger capillary is then also sealed, using a small blast flame, and the glass kept soft by holding it in the flame until a hollow bulb about 5 to 6 mm. in diameter (0.06- to 0.1-ml. capacity) forms, *E*, owing to the increased pressure of the heated air within. The size of the bulb will depend upon the length of time that it is kept in the flame. Excessive heating must be avoided, since this will gradually enlarge the bulb to the point of bursting. When cool, the tip of the fine capillary is broken off. The stem of the fine capillary at a point 1 to 2 cm. from the larger capillary is softened by heating in a luminous flame, and bent to an angle of about 45°, *F*. The distillation capillary is now ready for use.

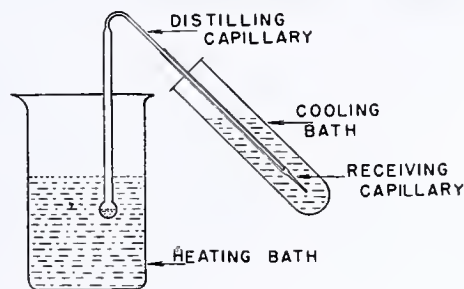


FIGURE 2

### Filling the Distillation Capillary

The drop of liquid to be fractionated is introduced into the distillation capillary in the following manner:

The bulb of the distillation capillary is warmed by immersing for a few moments in boiling water. While the bulb is still warm, the fine capillary tip is dipped into the drop of liquid to be fractionated, and then a cooling bath (solid carbon dioxide and acetone) is applied to the bulb. The decreased air pressure within, due to the cooling, causes the liquid to flow up the fine capillary, down the larger capillary, and into the bulb of the apparatus. Should any of the liquid remain in the stem, it is easily forced into the bulb by shaking the apparatus two or three times, as is customary with clinical thermometers. For a successful distillation the bulb should not be more than half full of liquid. In order to remove all traces of adhering liquid from the fine capillary arm, the arm is carefully warmed, while the bulb containing the bulk of the liquid is kept in the cooling mixture.

### The Distillation

A test tube, 6 cm. long, partly filled with ice water is used to cool the distillate-receiving capillary. For very low boiling liquids (30° C. or less) a small Dewar flask containing liquid air is used.



A capillary, 9 cm. long, having an inside diameter just a trifle larger than the outside diameter of the fine arm of the distillation capillary, is introduced into the cooling bath, with its sealed end resting on the bottom of the test tube. The fine stem of the distillation capillary is introduced into the receiving capillary as far as it will go. The entire setup is held by means of the water-containing test tube during the distillation. The bulb of the distillation capillary is now inserted into cold water contained in a small beaker. The water is then gradually and very slowly heated until a ring of condensate is seen rising up the column and condensing in the receiving capillary. At this point the flame should be at once removed, in order to keep the temperature of the water from rising too high. The distillation meanwhile is allowed to continue until a layer not more than 2 mm. thick (0.01-ml. volume) has collected in the receiving capillary. At this point the distillation capillary is quickly withdrawn from the receiving capillary by means of a glass rod supporting the curved part of the distillation capillary, and the bulb is quickly placed in the solid carbon dioxide-acetone cooling mixture, in order to suck back into the bulb any liquid remaining in the capillary portion of the apparatus.

The receiving capillary containing this first fraction is stored in the cooling mixture until ready for identification tests, such as the boiling point determination. Fractional distillation of the remaining liquid in the bulb is then continued as described above. Not more than 2 mm. of each fraction should be collected in the receiving capillaries. Five to six fractions can be obtained in this way from 0.06 ml. of liquid.

### Results Obtained by Fractional Distillation

Various mixtures of low boiling liquids were prepared, and small volumes, as indicated in Table I, were fractionated by the method described. The boiling points of the several fractions were determined by Emich's boiling point micro-method (1). The first fractions contain the lower boiling liquid, and the last fractions the higher boiling liquid, in a form pure enough to be identified by their respective boiling

TABLE I. EXPERIMENTAL RESULTS

Ml.	Mixtures of Liquids Used	Boiling Points of Pure Liquids ° C.	Expt.	Boiling Points of Successive Fractions ° C.	
0.02	Ethyl ether	34.5	1	34.5, 35.0, 49.5, 55.8	
0.02	Acetone	56.5	2	34.5, 35.3, 43.0, 55.5, 56.0	
0.03	Methyl alcohol	64.6	1	33.0, 35.5, 37.0, 41.5, 60.5, 63.5	
0.03	Methyl formate	31.5	2	32.0, 33.5, 38.5, 42.5, 63.2, 64.0	
0.03	Ethyl ether	34.5	1	21.5, 21.5, 22.0, 33.0, 34.0	
0.03	Acetaldehyde	21.5	2	21.0, 21.0, 22.5, 33.5, 34.0	
0.03	<i>n</i> -Propyl chloride	46.4	1	37.5, 37.5, 42.5, 43.5, 45.0	
0.03	<i>Iso</i> -Propyl chloride	36.5	2	36.0, 37.0, 40.5, 44.0, 46.5, 46.8	

points. The intermediate fractions contain mixtures of the two liquids.

If it becomes desirable to redistill some of the fractions, they may be introduced into the bulb of the apparatus as described and refractionated.

For corroborative identification, since there is no loss of material during the boiling point determination, the liquid in the receiving capillary can be used to determine its molecular weight by the method of Niederl *et al.* (2).

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## Modified Beilstein Test for Halogens in Organic Compounds

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THE well-known Beilstein test (1) for detecting halogens in organic compounds often gives positive tests for small amounts of halogen when actually none is present—for example, strong positive tests are obtained with certain types of pyrimidines, pyridines, and oxyquinolines (1).

Modified tests (2, 3) have been described for gases and volatile liquids.

A method has been in use in this laboratory for about 5 years which accurately detects the presence of halogens in organic compounds. With experience the operator may approximate the halogen to within 20 per cent of the actual value. The test has never given positive results on any compound not containing halogen, with the exception of materials containing copper.

A section of Monel metal tubing 0.9 cm. (0.375 inch) in outer diameter is heated to a cherry red color with a Bunsen burner equipped with a fishtail. The compound to be tested is brought up to within 1 cm. of the under side of the Monel tube. The material decomposes in the flame and the decomposition products are automatically swept up against the hot metal. If the compound contains halogen, a colored flare will appear which may

range anywhere between green and blue. The approximation of percentage is made possible by taking given amounts of material. The liquids are picked up on a platinum loop; the solids, on a small platinum spoon about 2 mm. in diameter.

It is necessary to learn to judge the amount of flare. Some compounds decompose very rapidly, giving one broad flare for only an instant, while another of the same halogen content may decompose more slowly and give a narrower flare over a longer period. With experience or the aid of control samples the operator may determine the percentage of halogen to within a very practical limit, so that it is possible, for instance, to differentiate easily between a 2 and 6, 5 and 10, or 25 and 50 per cent value. The method has proved of great value where a rough quick control is desired to follow the course of a reaction.

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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Particle-Size Distributions of Pigment Suspensions

### Determination with a Beaker-Type Centrifuge

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A method for the determination of the extent of disaggregation of pigments dispersed in aqueous and organic vehicles has been developed for particle sizes of 0.1 micron and above. The theoretical considerations of Romwalter and Vendl served as the basis for calculating the particle size distribution from a sedimentation curve obtained with a laboratory beaker-type centri-

fuge. Results are presented for a typical paint dispersion of a titanium dioxide pigment. To comply with industrial requirements, a rapid continuous method for the determination of size distributions from sieve through subsieve sizes is described for titanium dioxide pigment suspended in water. Illustrative data and additional possibilities for application are included.

THE particle size distributions obtainable under practical dispersion conditions are of fundamental importance in the application of finely divided materials for a wide variety of pigmentation purposes. Inherent in this are physico-chemical problems, the consideration of which necessitates quantitative methods designed for the determination of the completeness or extent of disaggregation of pigments suspended in aqueous or paint vehicles.

Although there exist considerable information and a voluminous literature on microscopic particle size measurements, these are subject to the following quoted limitations (3): "1. To obtain a satisfactory field for projection or photography, the mount should not be more than a few particles thick. This requires pressure on the cover glass or some other method of rubbing out the sample to a very thin layer and on such small amounts of material the procedure may result in a greater degree of deaggregation than it is possible to attain by the usual methods of commercial dispersion . . . . . In most cases, the particle size as observed microscopically will be at considerable variance with the effective particle sizes in an oil or rubber dispersion. . . . 2. In the case of nonuniform materials, difficulty is experienced in bringing both coarse and fine particles into focus at the same time. The lack of uniformity experienced in many pigments makes the method extremely laborious because of the necessity of measuring a large number of particles in order to obtain truly representative data." Then also (24), "Due to the optical fringes which appear on the particle images, it is dangerous to rely upon microscopic measurement in the range of 0.2 or 0.3 micron."

When this investigation was initiated, a literature survey showed that sedimentation methods offered interesting possibilities for eliminating the preceding objections, providing cognizance was taken of the colloidal principles involved in the preparation of stable suspensions. Thus, it was possible to avoid either the slow or rapid formation of flocculates (2). No difficulties were experienced with titanium dioxide as long as the dispersion technique and the medium were compatible with the wetting properties of the pigment. In the following, it will be assumed that aqueous suspensions were formed with a water-dispersing grade of titanium dioxide, whereas paint systems were made from oil-wetting pigments.

#### Sedimentation Methods

Since settling methods employing gravitational force have been well established, a procedure similar to that of Andreasen (3) was applied to a titanium dioxide dispersed with a high-speed mixer. The initial concentration of the suspension was 5 per cent.

The equivalent diameter was calculated from Stokes' law (Equation 1). A and B (Table I) denote the addition be-

TABLE I. GRAVITATIONAL SETTLING OF TITANIUM DIOXIDE  
SUSPENDED IN WATER

Settling Time Hours	Diameter Microns	Initial Pigment in Suspension	
		A %	B %
24	1.5	94	60
72	0.9	83	0.5
162	0.6	57	0.5



fore mixing of 0.1 and 1.0 per cent, respectively, of sodium silicate (pigment basis) whose alkali-silica ratio was 1 to 3.86.

It was observed that a dispersed titanium dioxide resisted settling while an excess of silicate produced rapid settling because of flocculation. However, because of the small sedimentation rate, differences in size distributions of good dispersions could not be measured with certainty. Another serious objection was the time interval of one week. To eliminate these, centrifugal force was substituted so as to increase the sedimentation velocities in accordance with a relationship derivable from Stokes' law.

$$Vg = \frac{d_1 - d_0}{18n} D^2 g \quad (1)$$

$$Vc = \frac{d_1 - d_0}{18n} D^2 W^2 X \quad (2)$$

$$Vc/Vg = \frac{W^2 X}{g} = R.C.F. \quad (12) \quad (3)$$

$Vg$  and  $Vc$  = the gravitational and centrifugal sedimentation velocities

$d_1$  and  $d_0$  = specific gravities of the pigment and suspension

$n$  = coefficient of viscosity of the medium

$D$  = the equivalent diameter of the particle of average weight

$W = 2\pi N/60$  where  $N$  is number of revolutions per minute

$X$  = distance in cm. of the particle from the axis of rotation

$R.C.F.$  = the relative centrifugal force

**CENTRIFUGAL SEDIMENTATION.** Centrifugal forces of varying magnitudes are experimentally available. Therefore, particle sizes amenable to centrifugalization have to be arbitrarily divided into (1) colloidal dimensions consisting of diameters from 0.1 micron to molecular dimensions, and (2) suspensoid sizes with a lower extreme at 0.1 micron and an upper limit with aggregate sizes of 30 microns.

The first group has been the subject of a large number of investigations by Svedberg (22), whose technique was employed by Nichols and Liebe (16) to determine the size distribution of lithopones dispersed in glycerol. A rutile titanium dioxide-glycerol suspension has also been studied with the same method to give the size distribution results of Kubelka and Srbe (13). A negligible quantity of material, less than 0.1 micron, was recorded. Table V contains the distribution values for a typical anatase type pigment. As a result, titanium dioxide pigment sizes could be given as primarily within the second category.

The individual particles or aggregates (2) referred to in this classification are sedimented conveniently with a beaker-type centrifuge, the application of which to monodispersed sols has been described by Hahn (11) and Schlesinger (20). Many materials, however, form polydispersed systems. Marshall (14) with a beaker-type centrifuge studied clays 2 microns and less in size. While the present investigation was being completed, Norton and Speil (17) published results on various clays also sedimented with a laboratory centrifuge. A range of 30 to 0.05 micron was covered, but the determinations required "two or three 8-hour days." In 1935, Romwalter and Vendl (19) presented the following theoretical basis for the calculation of a particle size distribution from a sedimentation curve obtained with a beaker-type centrifuge.

### Theoretical Considerations

If a polydispersed system is sedimented, after a time,  $t$ , the settled material can be divided into two parts: (1) a portion consisting of particles with diameters equal to or greater than  $D$ ; (2) the remainder, consisting of those particles which were sedimented even though their diameters were less than  $D$ . The theory for the evaluation of these two fractions from gravitational settling has been developed and confirmed by Odén (18). The validity of the application of Odén's

method to a sedimentation curve obtained with a beaker-type centrifuge has been established mathematically by Romwalter and Vendl:

$$\frac{1}{4.60 \log R/S} \frac{R^2 - S^2}{S^2} t \frac{dp}{dt} = \int_0^D F(D) dD \quad (4)$$

$p$  = mass of material sedimented after a time,  $t$

$R$  = distance from the axis of rotation to the bottom of the centrifuge tube

$S$  = distance from the axis of rotation to the meniscus of the suspension

$$D = \frac{6}{W} \sqrt{\frac{n \ln R/S}{2(d_1 - d_0)t}} \quad (5)$$

Since in any experimental work  $S$  and  $R$  are made constant, the left member of Equation 4 reduced to  $Ktdp/dt$ . This can be evaluated by applying Odén's method of tangential intercepts to the centrifugal sedimentation curve. Next, the amount of particles is obtained for a given diameter interval. The calculation is extended to include the entire range of sizes and, finally, the results are expressed as a particle size distribution.

### Size Distribution of a Titanium Dioxide-Glycerol Suspension

As a preliminary experiment, it was decided to examine a size distribution which overlapped the range in which microscopic size frequency measurements could be made with little difficulty. With this in view, a titanium dioxide pigment sample was suspended in a 91 per cent glycerol-water medium. The procedure was such that the suspension was formed with minimum work on the pigment. To ensure conditions of free settling of the particles, the final suspension contained 0.1 per cent of pigment.

**DETERMINATION OF THE SEDIMENTATION CURVE.** In the theoretical treatment previously outlined, one assumption was tacitly made that the centrifuge be free from vibrations. This requirement was satisfied in an International clinical centrifuge manufactured by the International Equipment Company. Although the centrifuge was in a constant-temperature room during sedimentation, the bowl temperature varied markedly, owing to the heat dissipated in the rheostat control. By removing the resistance from the immediate vicinity of the centrifuge and with the aid of the room controls it was possible to fix the temperature at  $22.5^\circ \pm 1^\circ \text{C}$ . The centrifuge speed was 1300 revolutions per minute. The centrifuge tubes were flat-bottomed vials with a diameter of 15 mm. and a height of 35 mm. To obtain a constant height, each tube was equipped with a scale, and by means of a magnifying glass 29 mm. of suspension were used for each sedimentation interval.

**SEDIMENTATION PROCEDURE.** A tube filled with suspension was placed in the centrifuge for  $t$  minutes, after which it was removed to a special holder so that with a capillary pipet, all of the suspension above 2 mm. from the bottom could be drawn off. The content of the pipet was washed into a 250-ml. beaker and slowly evaporated to dryness. To this, 10 ml. of concentrated sulfuric acid and 5 grams of ammonium sulfate were added. Boiling to dissolve the titanium dioxide produced discoloration, which was removed by the addition of a few drops of nitric acid. Dilution to 100 ml. in a volumetric flask followed. A portion was transferred to a Nessler tube, to which 5 ml. of 3 per cent hydrogen peroxide and sufficient distilled water for dilution to the 50-ml. mark were added. The yellow coloration produced was matched by mixing known amounts of a standard solution (1 ml. = 0.10 mg. of titanium dioxide) to a blank containing 5 ml. of hydrogen peroxide. A series of known dilutions were analyzed colorimetrically, and changes in titanium dioxide content could be measured with an accuracy of  $\pm 2$  per cent. Each tube was weighed before sedimentation and after removal of the suspension. With the initial concentration known and also the analyses, the percentage weight sedimented could be calculated. The results for all the values of  $t$  were collected in the form of a sedimentation curve.

**EVALUATION OF THE CONSTANTS OF STOKES' EQUATION.** The specific gravity ( $22.5^\circ \text{C}/22.5^\circ \text{C}$ ) of the glycerol-water



mixture was 1.2385, which according to Bosart and Snoddy (6) corresponded to a composition of 90.8 per cent glycerol. Interpolation of the tables of Sheely (21) gave 2.20 poises for the coefficient of viscosity. The specific gravity of titanium dioxide was taken as 3.90;  $\ln R/S = 0.362$ . Substitution of these values in Equation 5 gave:

$$D(\text{microns}) = 22.1/\sqrt{t}$$
$$t = \text{minutes}$$

(6)

Two completely independent determinations—i. e., preparation of suspension, centrifuging, colorimetric analysis, etc.—were performed. The agreement between the two sets of data is evident in Figure 1. Tangents were drawn at the indicated values of  $D$ . The successive differences in the tangential intercepts are incorporated in Table II.

The same suspension was placed in a counting chamber (30 microns in depth) and, with the aid of a microscope, the images of the particles were projected to a magnification of 8000 diameters. Table III contains the results of the microscopic count.

Tables II and III not only show data characteristic of each method but also permit the calculation and comparison of average weight diameters. Assigning the medium value for each class, the average particle size with respect to weight (microscopic)

$$\bar{D}_w = \Sigma nD^4/\Sigma nD^3$$

was 1.9 microns for the suspension under consideration. An average weight diameter for the distribution of Table II was calculated in accordance with a formula given by Gessner (10) and was equal to 1.6 microns. Considering the approximations made in the calculations, the above indicated fairly good agreement between the two methods of particle size analysis.

Size Distributions of Titanium Dioxide Dispersed in a Paint Vehicle

Because of the increasing importance of particle size distribution considerations in paints, the technique was altered to permit sedimentation studies of pigment-paint vehicle systems. The laboratory beaker-type centrifuge has been utilized in accelerated tests for the settling of pigments in paints (23).

TABLE II. PARTICLE SIZE DISTRIBUTION OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

Diameter Microns	Per Cent by Weight
>3.0	5
3.0-2.0	9
2.0-1.0	66
<1.0	20

TABLE III. SIZE-FREQUENCY OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

Diameter Microns	Number of Particles <i>n</i>
<1.0	1000
1.0-2.0	260
2.0-3.0	40
>3.0	2

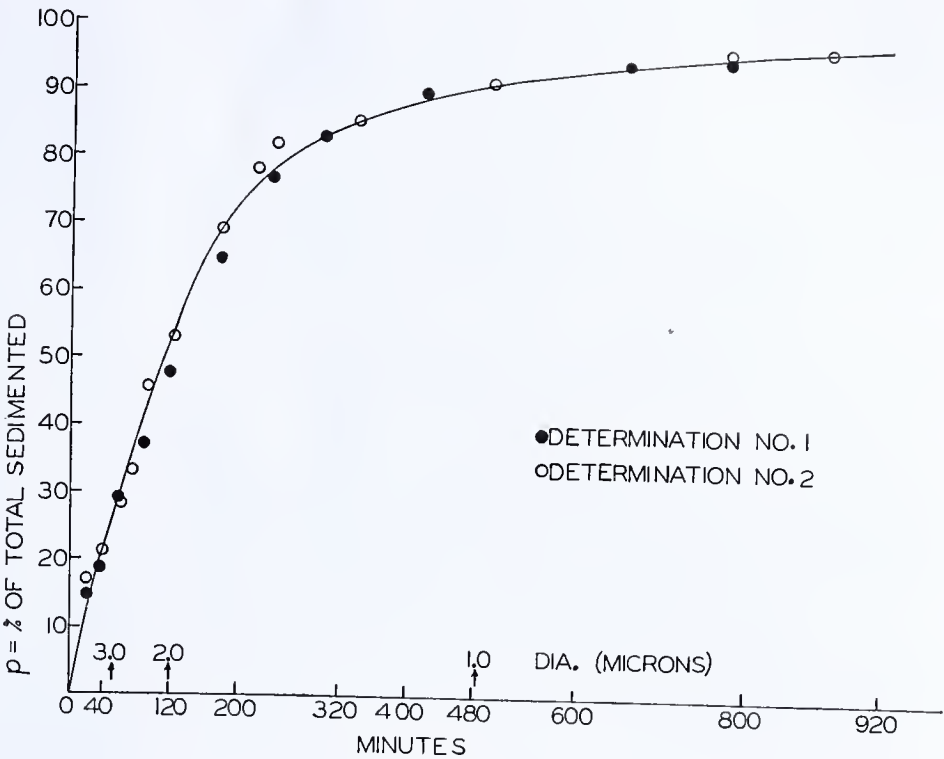


FIGURE 1. CENTRIFUGAL SEDIMENTATION OF TITANIUM DIOXIDE DISPERSED IN GLYCEROL

TABLE IV. PARTICLE SIZE DISTRIBUTION OF TITANIUM DIOXIDE DISPERSED IN A PAINT VEHICLE

Diameter Micron	Per Cent by Weight	Diameter Micron	Per Cent by Weight
>0.5	3	0.3-0.2	26
0.5-0.4	17	0.2-0.15	16
0.4-0.3	38		

**DISPERSION TECHNIQUE.** Two hundred grams of titanium dioxide were mixed with 108 grams of a special, prepared tung oil-linseed oil vehicle. (VM-1215 is well known to the paint trade and was developed by the Technical Service Laboratories of the Titanium Pigment Corporation, New York, N. Y.) This vehicle has excellent wetting properties and is recommended for titanium dioxide pigments in a wide variety of formulations. The paste was passed through a laboratory-size, three-roller mill whose setting was such that the rolls contacted with a minimum pressure. Three pastes were ground for the same pigment and each was diluted with mineral spirits to 5 per cent solids content.

**SEDIMENTATION PROCEDURE.** The final suspension was centrifuged at 1400 revolutions per minute in an International centrifuge (size 1). The speed was measured and controlled by means of an indicating hand tachometer to about  $\pm 10$  r. p. m. Wide mouthed, ground-glass-stoppered bottles 5.9 cm. (2.375 inches) in diameter and about 13.75 cm. (5.5 inches) high were employed, since they fitted snugly into the four centrifuge cups without any adjustments. After sedimentation, the suspension was poured into a beaker, stirred, and analyzed for titanium dioxide content. The gravimetric analyses for titanium dioxide were comparatively simple and rapid. A known weight of suspension in a tared crucible was taken and the volatile constituents were carefully evaporated until a charred residue remained. This was followed by calcination at 900° C. in an electric muffle. The ignited residue was weighed as titanium dioxide. Ash corrections were included.

The results of the sedimentations of three different suspensions of the same pigment were within  $\pm 5$  per cent of an average curve drawn through the values. The specific gravity (25° C.) of the final dilution of VM-1215 and mineral spirits was 0.85. An Ostwald viscometer (7) gave 0.015 poise for the viscosity of the mixture at 25° C. Since  $\ln R/S$  was 0.506, the result of numerical substitution in Equation 5 was

$$D(\text{micron}) = 1.87/\sqrt{t}$$
$$t = \text{minutes}$$

(7)

and the size distribution data are incorporated in Table IV.



With the foregoing data a fair estimate of the pigment surface can be made. Biddle and Klein (5) have published a formula for the surface associated with a given size distribution.

$$S = 6 \sum \frac{W\%}{\bar{D}} \quad (8)$$

$W\%$  = per cent weight of the total pigment for a given fraction

$\bar{D}$  = mean diameter for the size interval

$\Sigma$  = the summation of all the fractions within the size distribution

$S$  = surface area (square meters) for 3.90 grams or 1.0 cc. of titanium dioxide

The size distribution data of Table IV gave 20 square meters of surface, which corresponded to an average surface diameter of 0.3 micron.

The preceding determination can be used to advantage in paint studies, since variables in grinding, dispersion techniques, pigment properties, etc., may be evaluated in terms of the final size distributions. No attempt has been made to recommend an experimental technique. Instead, it is realized that a consideration of the specific properties of the suspension constituents, the available centrifugal equipment, and the nature of the problem to be investigated will suggest even more suitable procedures.

On the basis of some preliminary experiments, the application of the size distribution method is suggested for studying problems of compounding pigment in rubber. As an example, a titanium dioxide was incorporated into pale crepe rubber on a standard laboratory rubber mill. The pigment volume loadings could be varied from 10 to 15 per cent. After milling under constant conditions, the rubber mix was dissolved in toluene to produce a suspension of a given pigment content. This type of dispersion has been established by Gehman and Morris (9) with an ultramicroscopic technique. There remained the determination of the specific gravity and viscosity from which a centrifugal speed could be selected to give the required relative centrifugal force. A typical sedimentation curve was obtained and the particle size analysis made. Here again, it should be possible to evaluate the significance of milling variables by means of size distribution considerations.

In the manufacture and application of finished pigments, there arise size distribution problems, the solution of which by present methods involves an impractical expenditure of time and effort. It was felt that some importance could be attached to the development of simplified methods which were the result of a compromise between industrial requirements and those imposed by the fundamental principles of particle size measurements. Some final accuracy would have to be sacrificed. Nevertheless, it should be possible, for all practical purposes, to keep the precision losses within tolerable limits. The next section illustrates the feasibility of the aforementioned for an isolated case—namely, water dispersions of titanium dioxide.

### Determination of Particle Size Distributions of Titanium Dioxide Dispersed in Water

Experience with a variety of titanium dioxide-water suspensions (prepared by ball milling or high-speed agitation) has proved the existence of a range of aggregate sizes as well as varying particle size distributions. One extreme is determined by the retention on the 325-mesh sieve (44 microns). The other is in magnitude a few tenths of a micron. This wide range of sizes can be conveniently divided as follows:

1. Sieve fraction (44 microns and above)
2. Subsieve fraction
  - A. Gravitational sediment sizes (greater than 7 microns in diameter)
  - B. Centrifugal sedimentation sizes (less than 7 microns in diameter)

1. SIEVE FRACTION. Sieve measurements are well known and a procedure (1) can be recommended for this determination.

2. SUBSIEVE FRACTIONS. A. *Gravitational Sediment Sizes.* This fraction was measured by the sediment from the gravitational settling of a 5 per cent suspension containing 75 grams of pigment. The sedimentation was performed in a 2-liter beaker and the height was 12.5 cm. By means of Stokes' law, the smallest particle that could be completely settled out was calculated by

$$D(\text{microns}) = 36.4/\sqrt{t} \quad (9)$$

$t$  = minutes

for  $t$  = 30 minutes,  $D$  = 6.6 microns

On the completion of the sedimentation period, the suspension was carefully poured off from the sediment, which was reslurried to a height of 12.5 cm. and allowed to stand another 30 minutes. The resulting sediment was dried at 125° C. and weighed to give the "per cent of the total greater than 7 microns." With this figure and the "per cent retained by a 325-mesh sieve" subtraction gave the following: (1) per cent greater than 44 microns; (24) per cent between 44 and 7 microns.

If a more detailed analysis of fraction 2A is desired, it is readily amenable to microscopic examination. Another suspension batch is prepared and procedure 2A is repeated. Drying is omitted and instead a fixed quantity of glycerol is added with subsequent homogenization of the mixture. A portion is taken and diluted to a pigment content of 1 mg. per ml. of suspension. This is then examined in a Fuchs cell (depth = 200 microns) at 150 diameters' magnification. A glass disk with calibrated squares is inserted in the eyepiece and with the aid of a mechanical counter, it is comparatively simple to isolate and count the aggregates of about 10, 20, and 30 and above microns. A sufficient number of fields are taken at random to give a total observed volume of 1 cu. mm. or more, depending on the accuracy desired.

B. *Centrifugal Sedimentation Sizes.* Included in this group was the material remaining in suspension after the completion of the gravitational settling. The centrifugal equipment was the same as that described under the heading "Size Distributions of Titanium Dioxide Dispersed in a Paint Vehicle." However, the procedure differed in that only three centrifugal sedimentations at 350 revolutions per minute—i. e., 5, 45, and 120 minutes—were required. After each, the suspensions were siphoned from the well-caked sediments, stirred, and tested for specific gravity with a Westphal balance. Temperature corrections were introduced through the specific gravity of the medium. The specific gravity difference permitted an interpolation from a calibration curve of the per cent of titanium dioxide in suspension. Next, centrifugal time was converted into equivalent diameters after the substitution of the following in Equation 5:

$$\begin{aligned} 1.13 &\geq d_0 \geq 1.00 & d_1 - d_0 &= 2.8 \\ n &= 0.010 \text{ poise} & W &= 36.6 & \ln R/S &= 0.506 \\ D(\text{microns}) &= 6.36/\sqrt{t} \end{aligned} \quad (10)$$

$t$  = minutes

Thus for 5-, 45-, and 120-minute intervals, the equivalent diameters were 3.0, 1.0, and 0.5 micron, respectively, and the corresponding value of titanium dioxide contents gave the material less than the calculated size. Successive subtractions of these percentages yielded the per cent weight for more than 3, 3 to 1, 1 to 0.5, and less than 0.5 micron.

The less than 0.5 micron fraction for some titanium dioxide dispersions comprised the bulk of the pigment. It was of interest to extend the centrifugal sedimentation to the range of "individual particle" size. Additional sedimentation of 63 minutes at 1400 revolutions per minute left in suspension material which was assigned to the fraction less than 0.2 micron. A substantiation (at least in order of magnitude) was found in the fact that this material was on the border or below the limit of resolution of the microscope with an Apochromat HI 60X objective (N. A. = 1.35). The theoretical resolving power for the system was 0.2 micron. Table V contains the complete size distribution of a well-dispersed titanium dioxide-water suspension.

The additional sedimentation at 1400 revolutions per minute was usually omitted, with the result that after standardization of the experimental procedure, four complete size distribution determinations could be readily made in a one-



man working day with a four-cup centrifuge. Once a complete set of size distribution data was available at 5 per cent titanium dioxide suspensions, it was observed that within narrow limits similar values were obtainable from the centrifugal sedimentation of dilutions to only 10 and 15 per cent. The viscosity also showed but little sensitivity to the increased pigment concentrations.

TABLE V. SIZE DISTRIBUTION OF TITANIUM DIOXIDE-WATER SUSPENSION

Diameter Microns	Per Cent by Weight
>44	0
44-7	Negligible
+3	2 ( $\pm 0.5$ )
3-1	5 ( $\pm 1$ )
1-0.5	18 ( $\pm 1$ )
0.5-0.2	74 ( $\pm 4$ )
<0.2	0.6

Since the preceding methods are dependent on Stokes' law, correct results can hardly be expected if the limits of validity of Stokes' law are exceeded. Critical radii considerations (15) are of especial importance. The calculations involved were performed and the sedimentation velocities used in this investigation satisfied the critical radii criteria.

Other materials, such as barium sulfate suspensions of varying degree of fineness, were submitted to size distribution tests. Ground ilmenite ores, in which sieve and especially gravitational settlings are the predominating fractions, have also come within the scope of the method. These particular materials have been singled out because of their importance to the titanium pigment industry.

There have appeared an ever-increasing number of surface active agents, many of which have been suggested as "wetting" or "dispersing" agents for pigments. As distinguished from the liquid-air interface, Bartell (4) has pointed out that there are "no reliable methods available for the measurement of the interfacial tensions at the solid interface. . . the methods as yet available are on the whole so difficult and time-consuming that they are not of general application." Therefore, the use of surface-active agents with pigments has been chiefly a matter of empiricism. If the action of these materials is viewed in terms of their efficacy in disaggregating pigments, it becomes possible to differentiate by the size distribution determinations between a wetting agent—i. e., one that lowers the surface tension of water without altering the aggregation—and a true dispersant for titanium dioxide. The latter not only increases the amount of fines at the expense of the coarser fractions but also imparts enhanced suspension stability or resistance to flocculation.

### Acknowledgment

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## Estimation of Gossypol in Crude Cottonseed Oil

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THE method of Royce (1) for the estimation of gossypol in crude cottonseed oils uses the reagent pyridine in precipitating gossypol with aniline. Royce assumes that the precipitate is dianilinogossypol and from its weight calculates the corresponding quantity of gossypol. This assumption and procedure are invalid, for the precipitate which is weighed and calculated when pyridine is used is dianilinogossypol with two molecules of pyridine of crystallization which can be driven off by heating to constant weight 18 to 24 hours at 110° C., depending upon the amount of precipitate.

To demonstrate this, 0.2 gram of gossypol dissolved in peroxide-free ether was added dropwise to a hot mixture of petroleum ether (b. p. 60° to 68° C.), aniline, and pyridine, digested at 55° C., and allowed to stand. The precipitate was transferred to a Gooch crucible with a small amount of pyridine, washed with small amounts of petroleum ether, and dried 5 minutes at 100° C. and over phosphorus pentoxide at room temperature. The precipitate was found by analysis to be dianilinogossypol-dipyridine. Calculated for  $C_{42}H_{40}N_2O_6 \cdot 2C_5H_5N$ : N, 6.77; found, 6.68 and 6.66.

Dianilinogossypol was prepared from gossypol with aniline alone without the use of pyridine. It was recrystallized from boiling benzene and dried at 100° C. for 2 hours. Calculated for  $C_{42}H_{40}N_2O_6$ : N, 4.19; found, 4.11 and 4.10.

The dianilinogossypol-dipyridine was also prepared from crude cottonseed oil. This contained from 5.89 to 6.24 per cent of nitrogen, being low because of some loss of pyridine of crystallization in washing and drying the precipitate. Royce's method is not satisfactory, as some of the pyridine of crystallization in the precipitate is lost in washing and drying.

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# The Solvency of Petroleum Spirits

## Resin Solvency of Commercial Spirits

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PETROLEUM spirits are used in the paint and varnish industry both for dissolving natural or synthetic resins at approximately room temperature, and as a chilling and thinning material to add to mixtures of resin and drying oil after cooking at high temperatures.

The term "solvency" has been used in the industry to cover all manifestations of solvent power. Spirits with high solvency would be expected to dissolve resins or varnishes with ease and give dispersions of low viscosity and high stability. Such a broad and indefinite use of the term is likely to lead to lack of clarity in thinking, and to misunderstandings between laboratories. Therefore, for this work the following terms have been adopted: "Resin solvency" is used to describe the solvent power of spirits for resins when dissolved at room temperature without the addition of any third material; "varnish solvency," the solvent power of spirits for heated mixtures of drying oil and of resin; "dilution limit," the limit to which a varnish may be diluted without obtaining immediate precipitation (11, 25); and "dilution stability," the stability in storage of dispersions of varnish containing less than the limiting quantity of spirits as judged on the dilution limit basis (25).

Since this is at best a complex set of phenomena, it was decided to investigate first the most simple solvency relation—the solvency of spirits for resin at room temperature without the addition of any third material, or the "resin solvency."

The present paper is limited to the presentation of a practical means for evaluating the resin solvency of commercial petroleum spirits with a boiling range of 300° to 400° F. (149° to 204° C.). ["Petroleum spirits" is the approved A. S. T. M. term for this product. The term "mineral spirits" may include coal-tar distillates (A. S. T. M. D288-36T).]

### Fundamentals of Resin Dispersion

In evaluating the solvency of spirits for natural or synthetic resins which are completely soluble, it seems both logical and straightforward to judge the solvency by measuring the properties of these resin solutions themselves. This basis of judging solvency is very different from the kauri butanol test (3, 4, 5, 13, 18, 23, 30) which actually measures the amount of petroleum spirits that can be added, without causing precipitation, to a butyl alcohol solution of a resin that is essentially insoluble in petroleum spirits. Both the butyl alcohol and the insoluble resin are foreign to the problem at hand—namely, the relative ability of petroleum spirits to wet, solvate, and disperse the molecules of spirit-soluble resins.

The fundamental physics involved in the solution or dispersion of nitrocellulose molecules has been discussed in some detail by McBain (19). The fundamental point is that the molecules of the solvent must penetrate between the long chains of the nitrocellulose structure and have the ability to adhere more tenaciously to the molecular surface of the nitrocellulose chains than these chains can adhere to each other. Since soluble resins are now known to consist mainly of long-chain structures (10, 14, 27), this general picture should apply to all resins as well as to nitrocellulose. Furthermore, since different parts of the resin molecules usually consist of different type groups or linkages, a mixed solvent is usually able to wet and solvate the long chains more efficiently because each linkage or group in the chain can find in the solvent the

appropriate molecule of solvent (generally one of similar chemical type) to wet and solvate it. Therefore, in a perfect resin solvent the long chains become entirely separated from one another and the average or effective chain length is a minimum.

Staudinger has discussed the influence of chain length on viscosity and has shown that in both dilute (27) and concentrated solutions (27, 29), viscosity increases with length of chain for any given weight per cent concentration. It is, therefore, reasonable to believe that the relatively high viscosity observed when resins are dispersed in poor solvents is due to the tendency of the resin molecules to adhere to, or associate with, one another, thus increasing the effective chain length. That such association may be relatively stable in the case of molecules containing polar groups ( $-\text{COOH}$ ,  $-\text{OH}$ ,  $\text{C}=\text{O}$ ,  $-\text{NH}_2$ , etc.) dissolved in nonpolar solvents has been known for a long time. For example, it was reported years ago in the thorough text of Biltz (6) that the molecular weight of benzoic acid in benzene determined by either the freezing or boiling point method is nearly double the true value, showing clearly the existence in this case of association, even at the boiling point of benzene. Similar results have been obtained in this laboratory with long-chain organic acids such as oleic acid, stearic acid, and naphthenic acids in nonpolar solvents.

To sum up, a good solvent provides molecules capable of wetting and solvating all parts of the long-chain resin molecules, so that these long-chain molecules will have little tendency to associate with one another.

The fundamental studies of Staudinger (27, 28, 29), McBain (19, 20, 21), and Kraemer (14), therefore, provide strong support for the opinion of many workers (2, 9, 12, 22, 24, 26, 31, 32), that a "high solvency" solvent will give resin solutions of relatively low viscosity at any chosen concentration. In several recent publications (8, 23, 31) both viscosity and miscibility criteria of solvency are discussed. In the strictly practical papers of Ware and Teeters (32), and of Mantell and Skett (22), dependence upon viscosity data is advocated as a basis of judging solvency.

The barrier which now appears to prevent a clear understanding among various workers of the nature of "solvency" is the habit of using terms such as "solvent strength," "solvent power," or "solvency" (4, 12, 13, 18, 24, 30) as though they described a definite property like density or refractive index which should be the same independent of the manner in which it is determined. Actually "solvent power" is a meaningless term unless we specify what is being dissolved. There is no a priori reason for believing that "good solvency" as judged by the kauri butanol test will enable one to predict good solvency on the basis of a viscosity test with ester gum, dammar, Pliolite, or phenolic or alkyd type resins. Toby (31) says, "For each individual plant problem it is my thought that the viscosity of that specific gum employed should be tested with every projected solvent, as this will give us the most accurate and pertinent information for each specific need." The authors agree with this point of view, but feel that the problem can be simplified to a certain extent by studying the response of typical resins to a representative selection of technical solvents.

It was decided to confine this preliminary investigation to commercial petroleum spirits and to four types of spirit-



soluble resins, placing more emphasis upon variety of chemical types than on whether or not these resins are used commercially on a cold-cut basis. The resins actually used are as follows:

1. Straight phenolic and modified resins
  - A. Straight phenolic resins (also called "pure" or "concentrated" phenolic resins)
    - Super-Beckacite<sup>1</sup> 1001 (Reichhold Chemical Co.)
    - Amberol ST-137 (Resinous Products & Chemical Co.)
  - B. Modified Phenolic Resins
    - Beckacite 1100 (Reichhold Chemical Co.)
    - Amberol F-7 light (Resinous Products & Chemical Co.)
2. Ester gum
  - Ester gum 6 (American Cyanamid Co.)
  - Synthe Copal (Reichhold Chemical Co.)
3. Alkyd resin
  - Glyptal 2454 and 2464 (General Electric Co.)
4. Thermoplastic rubber
  - Pliolite (Goodyear Tire & Rubber Co.)

### Procedure

In planning the "resin solvency" portion of this general investigation of solvency, it was decided to choose a procedure which would make possible reproducible and precise viscosity measurements on resin solutions. Therefore, dissolving the resin by refluxing or otherwise heating the solvent and the resin was not seriously considered, because of the possibility of losing the light ends of the solvent, and the probability that it would be difficult to control with sufficient exactitude the effect of time and temperature of heating on the resin itself.

The procedure chosen, after some preliminary investigation, is as follows:

A clean dry 8-ounce (240-cc.) bottle is weighed to the nearest 0.05 gram using an accurate pan balance (Arthur H. Thomas Co., No. 1907, is suitable). Then 50  $\pm$  0.05 grams of solvent are weighed into the bottle, making the final adjustment by adding solvent to the bottle on the balance by means of a pipet. Finally 50  $\pm$  0.05 grams of freshly ground resin (grinder, A. H. Thomas No. 4265) are weighed on a glazed paper and added to the solvent in the bottle. The resin should be ground sufficiently fine to assure uniform dispersion of the material, but should not be ground to the consistency of a flour, because of difficulty in handling it in that state. The last of the resin usually adheres to the paper and must be brushed in with a camel's-hair brush. In case a concentration of more or less than 50 per cent is wanted, the appropriate weights of resin and solvent are taken, but the weight of the whole batch is kept at 100 grams.

As soon as the resin has been added, the bottle is tightly corked and then immediately placed in a shaking machine (A. H. Thomas No. 8916) with the bottle horizontal and lying lengthwise with the motion of the shaker. This shaker operates with a 7.5-cm. (3-inch) stroke, approximately 360 strokes per minute (180  $\pm$  20 r. p. m. on drive pulley). Solution will usually take place overnight, 17 to 24 hours, but in a few cases, a longer time may be required. After solution is complete, the bottle should be centrifuged or allowed to stand until any lint or dirt in the resin solution has settled out.

The viscosity is measured at 77° F. (25° C.) using precision kinematic viscometers such as those designed by Fenske and co-workers (1, 33).

In order to obtain very reliable data for the present investigation, two bottles of solution were prepared in each case, and the viscosity of each mix was determined in a different viscometer. If the viscometers checked within 2 per cent, the average was accepted; if the check was not so good, the viscosities were re-checked.

The agreement of the data from sets of viscometers having capillary tubing of widely different diameter, and times of out-flow differing about tenfold, indicates that the deviation from Poiseuille's law is small or nonexistent for these dispersions. The data show that the viscosities are true viscosities at least for the limited range of shearing stress represented by the authors' viscometers.

<sup>1</sup> In the balance of this paper and in that following (17), the prefix "Super" before Beckacite 1001 has been omitted.

In the practical determination of resin solvency, it is desirable to adjust the concentration of the resin so that the viscosity in the standard blend will be in the range of 200 to 500 centistokes. The worst solvents, which are seldom below 30 resin solvency, will then not be over 1000 to 1700 centistokes, depending on the resin. In this range, mixing on the shaking machine is satisfactory, as are flow and drainage in viscometers of the Fenske or similar type. It is also recommended that concentrations be chosen at 5 per cent intervals—i. e., 40, 45, 50, 55, 60, 65, etc.

In the field of the straight phenolic and modified phenolic resins, Beckacite 1001 is very satisfactory from the point of view of uniformity, stability over long periods of time (Table IV), ease of dispersion, and reproducibility of viscosity measurements and is, therefore, recommended as the standard resin for this general field. Amberol ST-137 is similar to Beckacite 1001 and appears to be suitable for routine resin solvency work, but it has not yet been as thoroughly investigated as Beckacite 1001.

In the case of ester gum, either ester gum 6 or Synthe Copal may be used. These resins appear to be somewhat less uniform than the phenolic resins, and there is a pronounced tendency for change after grinding. The ester gum should, therefore, be ground on the same day that it is to be used and should be thoroughly mixed after grinding. These ester gums give almost identical viscosities.

Glyptal 2464, without added solvent, was very gummy and sticky and changed on exposure to air. Therefore, enough mixes were always planned to use up a whole can within a few hours of the time it was first opened. A wide-mouthed bottle must be used in preparing mixes with these resins. Reproducible results can be obtained with this resin, although more skill is required than with the other resins mentioned. Fifty to 60 per cent resin is about the right concentration for the alkyds thus far studied.

Pliolite resin is supplied in small hard pieces which are too tough to grind and, as received, are small enough to dissolve. This resin is uniform and is stable in storage for reasonable periods of time, probably because the condensation catalyst is thoroughly washed out in the process of manufacture (7, 16). Twenty per cent resin is sufficient in testing with Pliolite.

TABLE I. PHYSICAL PROPERTIES OF STANDARD BLEND (SOLVENT 1) AND CONSTITUENTS THEREOF

	Standard Blend	Diethylbenzene <sup>a</sup>	Decahydronaphthalene <sup>b</sup>	Isooctane <sup>c</sup>
A. P. I. gravity at 60° F.	40.5	31.0	27.6	71.4
A. S. T. M. distillation:				
Initial boiling point, ° F.	215	345	365	204
5%	232	347	368	206
10%	248	348	369	207
50%	353	350	372	208
90%	363	352	374	210
95%	367	353	376	210
End point	383	380	392	248
50% boiling point corrected for emergent stem: ° F.	360	357	380	209
° C.	182	180	193	98
Density, d 20/4	0.8185	0.8674	0.8867	0.6918
Refractive index, $n_D^{20}$	1.4566	1.4965	1.4780	1.3921
Refractivity intercept	1.0473	1.0628	1.0346	1.0461
Specific dispersion $\times 10^4$	123	161	99	102

<sup>a</sup> Dow Chemical Co.

<sup>b</sup> Du Pont Co., technical grade.

<sup>c</sup> Isooctane, technical, reference fuel F, Standard Oil Co. of N. J.

### Standard Solvent

The choice of a standard solvent for this work presented some difficulty. In view of the fact that two widely used commercial petroleum spirits contained approximately equal proportions of aromatics, naphthenes, and paraffins, it seemed reasonable to use as a final standard a three-component blend of aromatic, naphthenic, and paraffinic compounds of technical purity. Diethylbenzene (Dow Chemical Company), decahydronaphthalene (Eastman No. P1905 or du Pont), and isooctane (reference fuel F, Standard Oil Company of New Jersey) are all available in a reasonably pure state.



The molecular volumes of these compounds are, respectively, 154.5, 155.5, and 165 cc.; therefore, blending equal parts by volume will give approximately equal parts on a mole per cent basis. This equal-volume blend was chosen as the reference standard and is designated throughout this paper as solvent 1. Its properties, and the properties of its constituents, are given in Table I. Solvent 1 is not intended for routine use, but merely as a standard liquid of constant solvency which can be used to calibrate selected samples of petroleum spirits which can then be used as working standards.

The value of 100 is assigned to solvent 1 merely as a basis for arriving at reproducible comparative values.

### Resin Solvency

The work of McBain and of Staudinger leads one to expect that a good solvent for a particular resin will separate the molecules of the resin from one another and produce a dispersion of minimum viscosity. In Figure 1, A, viscosity data for dispersions of a straight phenolic resin (Beckacite 1001) are plotted against the kauri butanol number of the solvents. Solvents 2 to 32, inclusive, are petroleum spirits; for most of these the properties are given in Table II. Solvent 1 is a standard blend of pure compounds, for which data are given in Table I. The left-hand scale in each case gives kinematic viscosity in centistokes; the right-hand scale gives viscosity in terms of Gardner-Holdt tubes (11), based on the absolute viscosity in poises specified for these tubes. Viscosities in poises were obtained by multiplying the kinematic viscosity

by the density of the resin solutions at 77° F. (25° C.). For the authors' solutions a good linear relation exists between kinematic and absolute viscosity; therefore, there is no inconsistency for these solutions in using both kinematic and absolute viscosity scales on the same graph. The density of the resin solutions for which the authors have thus far obtained density data fits the following approximate equation within about  $\pm 0.005$ :

$$\text{Density of resin solution at 77° F.} = \text{density of solvent at 77° F. (25° C.)} + 0.00288 \text{ weight per cent of resin} - 0.017$$

It is somewhat surprising that one equation will fit the data obtained for Pliolite, Beckacite 1001, Beckacite 1100, Amberol F-7, Glyptal 2464, and ester gum 6, and for solvents 1, 2, 4, 6, 7, 8, and 11.

The kauri butanol data shown were all carefully checked, standardization being against toluene and *n*-heptane (5).

In Figure 1, A, point 1 is standard blend 1. Spirit 2 is a commercial spirit, containing approximately equal quantities of paraffins, naphthenes, and aromatics, which was used as a working standard. Points 3 to 11, inclusive, are other commercial petroleum spirits of 300° to 400° F. boiling range. Solvents 2, 3, 5, 8, and 11 have kauri butanol values between 42 and 44, yet the viscosities of the solutions obtained with these solvents vary from 300 to 690 centistokes or from K<sup>+</sup> to U<sup>+</sup> on the Gardner-Holdt scale. These data show definitely that the kauri butanol test does not measure the ability of a spirit to wet, solvate, and disperse phenolic resins such as Beckacite 1001. Figure 1, B, C, and D show that the same

statement can be made concerning dispersions of ester gum, alkyd, and modified rubber (Pliolite) resins.

It was desired to obtain an index for solvency based on viscosity, but one which would be approximately constant irrespective of the concentration of the solution and at least approximately independent of the temperature at which the viscosity data were obtained. Such an index was obtained rather simply in the following manner, starting with the data shown in Figure 1, A.

If the viscosity of each solution is divided into the viscosity of Beckacite 1001 in standard blend 1 and then multiplied by 100, the values obtained are shown in Table III. Viscosity ratios relative to working standard 2 are also given. A comparison of the data for Beckacite 1001, Beckacite 1100, and Amberol F-7 shows that these three resins of the straight phenolic and modified phenolic types (15, p. 162) all rate these spirit samples in practically the same order.

It was, therefore, decided to give this viscosity ratio, relative to pure compound standard 1, the name "resin solvency" (R. S.) and define it by the following equation:

$$\text{R. S.} = \frac{\text{kinematic viscosity of solution of X\% resin in standard spirit 1}}{\text{kinematic viscosity of solution of X\% resin in spirits under test}} \times 100$$

The resin solvency, being based on a standard blend of pure compounds, can be reproduced at any future time and is therefore suitable for permanent record. For comparison of several commercial spirits, ratios of the resin solvencies can be

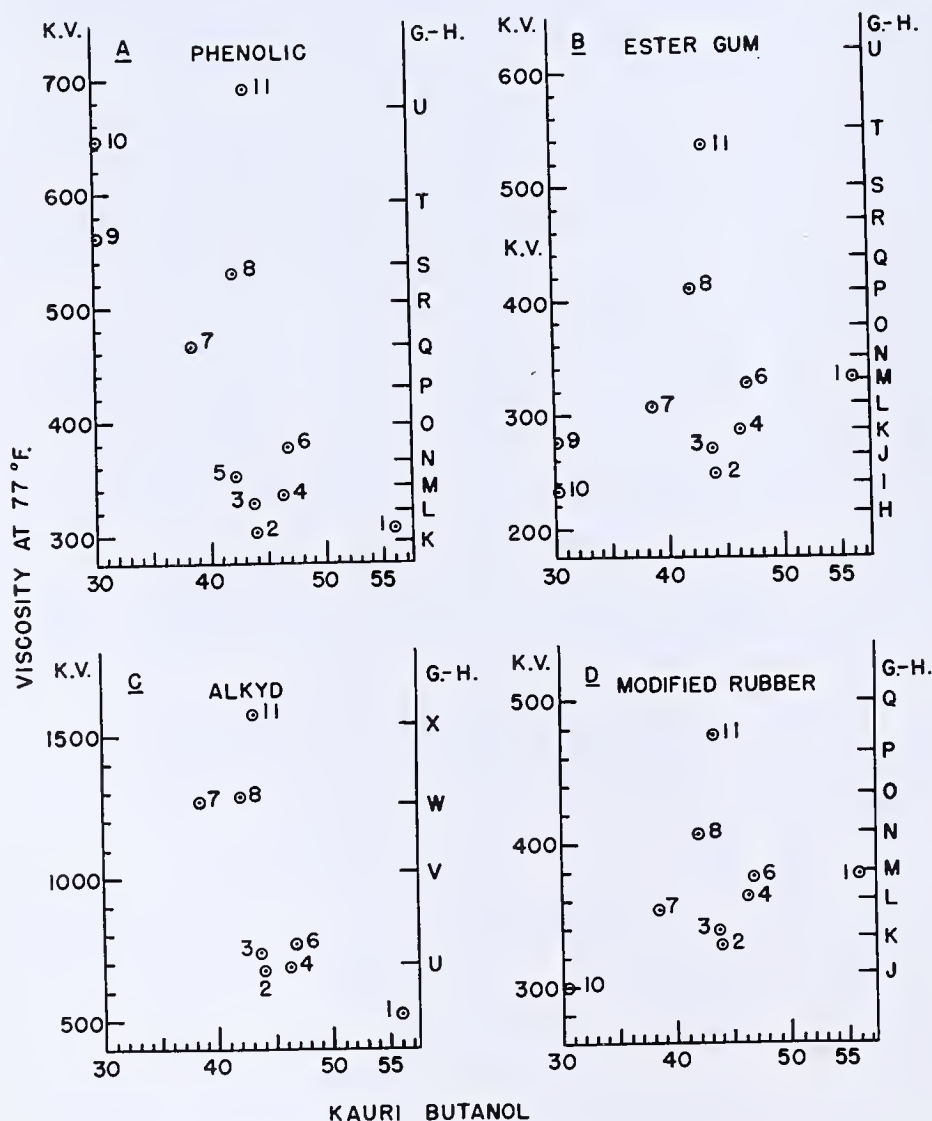


FIGURE 1. VISCOSITY OF RESIN SOLUTION vs. KAURI BUTANOL NUMBER OF SPIRITS



used—for example, relative resin solvencies (R. R. S.) based on spirit 2 are given in Table III for comparison with the actual resin solvency values.

Table III also gives the resin solvency, based on Figure 1, *B*, *C*, and *D*, for ester gum 6, Glyptal 2464, and Pliolite, respectively, and for Beckacite 1100 and Amberol F-7, for which graphs are not shown. It is clear that the resin solvencies of some solvents—e.g., 2, 3, and 4—are high with all these resins. Other solvents such as 8 and 11 are consistently low. Still other solvents are good for some resins and poor for others. For example, solvents 7, 9, and 10 are relatively good

solvents for Pliolite and ester gum 6, but are poor for the modified phenolic and alkyd resins.

The effect of concentration is shown in Figure 2, in which the resin solvencies based on pure compound blend 1 and relative resin solvencies based on spirit 2 are plotted for three concentrations of Beckacite 1001 and ester gum. In the case of both resins the relative resin solvency shows less change with concentration than the resin solvency. This means that the commercial petroleum spirit samples all have viscosity concentration curves of a similar type, whereas the viscosity concentration curve of the standard pure compound, blend 1, is

TABLE II. PHYSICAL PROPERTIES OF PETROLEUM SPIRITS USED FOR RESIN SOLVENCY DETERMINATIONS

Spirits	12	15	18	2	21	3	4	5	6	28	7	8
Resin solvency:												
Beckacite 1001	118	108	104	101	98	93	92	87	81	68	66	58
Ester gum 6	....	....	137	134	....	123	117	....	102	55	109	80
Glyptal 2464	....	....	....	77	75	71	75	....	68	....	41	41
Pliolite	....	....	117	115	113	111	105	113	100	....	107	93
Kauri butanol	44.6	44.1	43.0	44.0	43.3	43.7	46.4	42.1	46.9	66.4	38.5	42.2
Aniline point, ° F.	97.5	104.4	105.1	105.0	107.4	107.4	99.0	115	102	23.5	125	120
Density 20/4	0.7932	0.7940	0.7941	0.7927	0.7969	0.7958	0.8038	0.7928	0.8066	0.8641	0.7861	0.8024
Refractive index 20/D	1.4469	1.4472	1.4471	1.4472	1.4479	1.4479	1.4526	1.4452	1.4509	1.4882	1.4400	1.4447
Refractivity intercept	1.0503	1.0502	1.0499	1.0508	1.0497	1.0500	1.0507	1.0488	1.0476	1.0561	1.0469	1.0435
Specific dispersion $\times 10^4$	121	123	120	120	124	120	125	116	119	145	112	106
Solvent viscosity, centistokes:												
77° F.	....	....	....	1.051	....	1.080	1.105	1.069	1.125	....	1.141	1.184
100° F.	....	....	....	0.896	....	0.924	0.941	0.913	0.941	....	0.968	1.000
Engler distillation:												
A. P. I. gravity at 60° F.	46.0	45.8	46.0	46.1	45.2	45.4	43.7	46.1	43.1	31.5	47.6	44.0
Initial boiling point, ° F.	295	303	303	304	307	306	308	300	311	357	300	305
5%	308	313	314	316	319	317	318	314	319	366	316	316
10%	311	317	318	319	322	321	321	317	322	372	320	319
50%	324	329	331	333	336	336	341	333	336	383	338	336
90%	341	348	352	358	357	357	369	362	361	402	364	367
95%	346	353	361	368	368	367	382	374	377	410	380	379
End point	377	378	383	390	391	394	396	392	395	417	414	392

Spirits	9	10	11	32	Cuts of 21			Cuts of 8			
					0-20	40-60	80-100	0-20	40-60	60-80	80-100
Resin solvency:											
Beckacite 1001	55	48	45	30	157	102	51	73	56	50	32
Ester gum 6	121	142	62	56	....	....	....	....	....	....	....
Glyptal 2464	....	....	33	....	....	....	....	....	....	....	....
Pliolite	....	127	79	....	....	....	....	....	....	....	....
Kauri butanol	30.3	30.5	43.4	36.0	47	44.5	39	41.5	41.9	42.1	41.6
Aniline point, ° F.	140.2	149.0	119	132	93.2	102.6	122.8	122.2	118.6	118.8	122.0
Density 20/4	0.7730	0.7582	0.8065	0.8011	0.7920	0.7970	0.8005	0.7884	0.8003	0.8077	0.8184
Refractive index 20/D	1.4336	1.4268	1.4467	1.4485	1.4457	1.4482	1.4492	1.4380	1.4442	1.4480	1.4543
Refractivity intercept	1.0471	1.0477	1.0434	1.0479	1.0497	1.0497	1.0489	1.0438	1.0440	1.0441	1.0451
Specific dispersion $\times 10^4$	105	105	109	110	125.1	124.5	118.8	110.9	110.2	113.8	114.5
Solvent viscosity, centistokes:											
77° F.	....	....	1.263	....	....	....	....	....	....	....	....
100° F.	....	....	1.060	....	....	....	....	....	....	....	....
Engler distillation:											
A. P. I. gravity at 60° F.	50.6	54.1	43.1	44.0	46.3	45.2	44.4	47.1	44.5	42.9	40.6
Initial boiling point, ° F.	312	311	310	343	270	316	352	288	314	324	352
5%	320	319	319	358	284	322	356	297	320	334	361
10%	323	321	325	361	288	324	358	299	321	336	363
50%	340	339	340	387	306	330	366	311	330	344	371
90%	368	373	374	423	328	344	380	334	352	364	390
95%	378	384	387	438	335	352	390	349	362	372	400
End point	401	396	418	455	366	380	409	381	384	398	440

TABLE III. RESIN SOLVENCIES AND RELATIVE RESIN SOLVENCIES

Spirits	Straight Phenolic, 55%		Modified Phenolic				Alkyd, 50%		Rosin Ester, 65%		Modified Rubber, 20%	
	Beckacite 1001		Beckacite 1100		Amberol F-7		Glyptal 2464		Ester Gum 6		Pliolite	
	Standard	Working	Standard	Working	Standard	Working	Standard	Working	Standard	Working	Standard	Working
	blend	standard	blend	standard	blend	standard	blend	standard	blend	standard	blend	standard
	1	2	1	2	1	2	1	2	1	2	1	2
	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)
1	100	99	100	88	100	106	100	130	100	75	100	87
2	101	100	114	100	94	100	77	100	134	100	115	100
3	93	92	105	92	86	92	71	92	123	92	111	97
4	92	91	99	87	94	100	75	98	117	87	105	91
5	87	86	....	69	73	....	....	....	....	....	113	98
6	81	80	84	74	86	91	68	88	102	76	100	87
7	66	65	74	65	36	38	41	53	109	81	107	93
8	58	57	59	52	39	42	41	53	80	60	93	81
9	55	54	....	....	....	....	....	....	121	90	....	....
10	48	47	....	....	....	....	....	....	142	106	127	110
11	45	44	46	40	31	33	33	43	62	46	79	69
Kinematic <sup>a</sup> viscosity with standard 1	306	...	227	...	312	...	521	...	334	...	379	...

<sup>a</sup> Since different batches of the same grade of resin often differ somewhat, these viscosities are intended to show what authors obtained and are in no sense standard values.



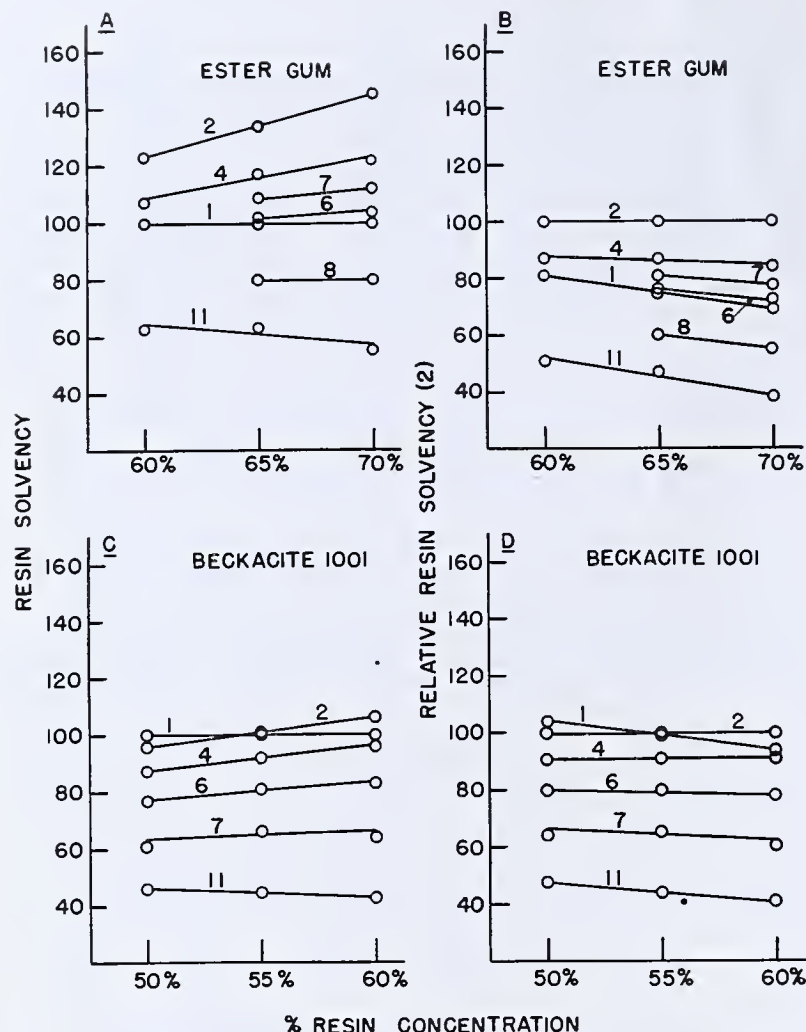


FIGURE 2. RESIN SOLVENCY AND RELATIVE RESIN SOLVENCY vs. RESIN CONCENTRATION

somewhat different. For the purpose of this work—namely, obtaining relative solvent power of various samples of commercial petroleum spirits—it is clear that the same order of solvency will be obtained irrespective of the concentration at which the comparisons are made. Data were obtained confirming this conclusion for Beckacite 1100, Amberol F-7, Glyptal 2454, and Glyptal 2464.

It is recommended that Beckacite 1001 be made up in 55 per cent concentration and ester gum 6 in 65 per cent concentration. For other resins, concentrations may be chosen on the basis suggested in the section on procedure.

The approximate constancy of the relative resin solvency at various concentrations makes it possible to construct a family of viscosity concentration curves such as those presented by Ware and Teeters (32). It is only necessary to have experimental data for the viscosity of the reference solvent at three concentrations and of the other solvents at one concentration. Curves drawn in this way based on the data for spirit 3 (resin solvency 93) with Beckacite 1001 in Table IV are shown in Figure 3. The viscosities of solvents 6, 7, and 11 are based on the relative resin solvency values in Table III. The seven experimental points on which this graph is based are shown as circles.

This graph is of interest since it shows clearly the difference between this work, in which viscosity ratios at one concentration (line X — Y) are compared, and the work of Ware and Teeters in which the concentrations at equal viscosity (line Y — Z) are compared. The order of solvency on either basis is the same.

The effect of temperature is shown in Table V, which contains data obtained at 77° F. (25° C.), 100° F. (37.8° C.), and 130° F. (54.4° C.). These data show that there is somewhat

TABLE IV. VISCOSITY vs. CONCENTRATION AND CONSTANCY OF VISCOSITY USING BECKACITE 1001<sup>a</sup>

Concentration % by Weight	Shipment of Resin	Date of Run	Kinematic Viscosity Spirit 3	Kinematic Viscosity Spirit 4	Kinematic Viscosity Spirit 11
50	First	4-8-38	119	118	230
			119	120	230
		4-19-38	117	117	225
	Second	4-28-38	118	117	226
			122	123	236
			122	123	236
55	Second	4-28-38	336	330	699
			328	330	695
		5-24-38	327	335	707
	Fourth	10-6-38	332	335	691
			327	335	672
		2-2-39	329	335	672
60	Second		325	..	700
			321	..	..
		5-24-38	953	973	2161
			965	969	2172

<sup>a</sup> One shipment of Beckacite 1001 gave lower viscosities but the same relative resin solvencies and was also constant in storage. It is desired to emphasize the constancy of each sample in storage rather than the absolute agreement between three out of four shipments of this resin.

less viscosity difference at 100° F. (37.8° C.) and 130° F. (54.4° C.) than at 77° F. (25° C.)—i. e., the relative resin solvency of a poor solvent is somewhat better at the higher temperature.

The small influence of temperature on resin solvency is in line with data of Staudinger (27, p. 207) for polystyrol of approximately 120,000 molecular weight in tetralin. These data are reported in terms of specific viscosity, but by algebraic transposition it can be shown that for solvents of approximately the same viscosity-temperature slope the resin solvency must be independent of temperature if the specific viscosity is independent of temperature. (Specific viscosity = relative viscosity — 1. Relative viscosity = viscosity of solution ÷ viscosity of solvent.)

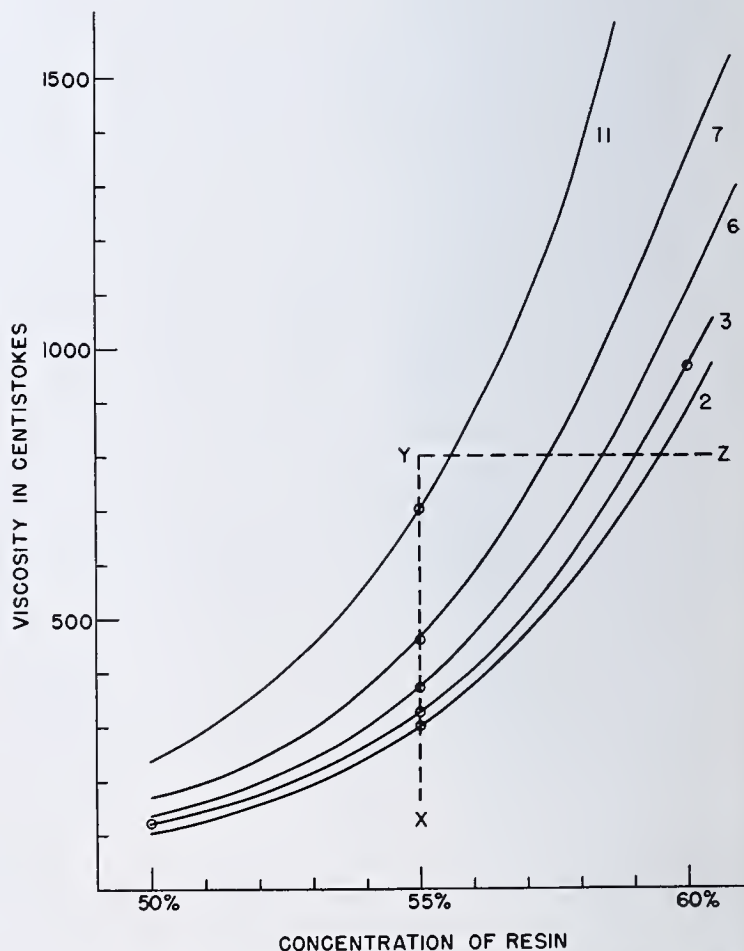


FIGURE 3. VISCOSITY IN CENTISTOKES vs. CONCENTRATION OF RESIN, PLOTTED FROM VISCOSITY RATIOS



TABLE V. EFFECT OF TEMPERATURE ON RESIN SOLVENCY OF SPIRITS

Beckacite 1001, 55% Resin, 45% Solvent									Ester Gum 6, 65% Resin, 35% Solvent						
Temperature °F.	°C.	Standard pure compound blend 1 K. V.	Spirit 18		Spirit 8		Ratio of resin solvency <sup>a</sup> 8/18		Standard pure compound blend 1 K. V.	Spirit 18		Spirit 8		Ratio of resin solvency <sup>a</sup> 8/18	
			K. V.	R. S.	K. V.	R. S.				K. V.	R. S.	K. V.	R. S.		
77	25	319	307	104	737	43	41	61	301	220	136	475	63	46	50
		319	307		736				300	218		477			
100	37.8	121	110	111	221	55	49	69	124.3	92.8	134	178	70	52	58
		122	110		219				124.5	92.8		177			
130	54.4	47.3	40	119	69	69	58	77	50.8	38.7	131	64.6	78	60	66
		...	40		69				50.8	38.7		64.9			
Change															
77-100° F.		...	...	+ 7	...	+12	+ 8	+ 8	...	...	-2	...	+ 7	+ 6	+ 7
77-130° F.		...	...	+15	...	+26	+17	+16	...	...	-5	...	+15	+14	+14

<sup>a</sup> Solvents 15 and 18 are of approximately balanced composition.

As a practical working temperature 77° F. (25° C.) was chosen, since it is slightly more selective and is fairly near room temperature in many laboratories during a considerable portion of the year. It would be possible, even though not particularly desirable, for a laboratory to determine resin solvency without a thermostat, provided the viscosities of both the standard and unknown were determined at the same time and the same temperature.

The data in Table V when plotted on the A. S. T. M. kinematic viscosity chart C (D341-37T) give good straight lines.

The data thus far presented show that the resin solvency for any spirit is little affected by the concentration of resin or by the temperature, but that there may be considerable difference in resin solvency determined with different classes of resins.

Molecular Concentration of Solvent

To determine the effect of boiling point on resin solvency, steam and fire distillations were made on two petroleum spirits of approximately balanced composition (3 and 21) and one petroleum spirit containing a large amount of naphthene (8).

Solutions containing equal weight per cent of resin were prepared with each series of cuts and with the original spirits. In Figure 4, A, the resin solvencies of the cuts relative to the original spirits in each series are plotted against the 50 per cent points of the A. S. T. M. distillations. All the points may be represented well by one curve, even though there is some scattering in the case of the four bottoms samples.

In Figure 4, B, curves are shown for cuts of petroleum spirits 8 and 21 made up with an equal number of moles of spirits per gram of resin. The molecular weights of these cuts of spirits were determined cryoscopically in benzene. Apparent molecular weights at three or more concentrations were obtained. The value used represents the extrapolated value corresponding to zero concentration. With the exception of the two bottoms, samples A and C, all the blends in each separate series had the same viscosity. Examination of the bottoms from spirit 21 revealed a slight difference in the per cent of aromatic hydrocarbon as compared with the other cuts of 21. Pure *p*-cymene was added to bottoms A to give it the same aromatic content as the other cuts of 21, and with this blend, point B was obtained, which is in line with the other points. The authors have not yet determined the reason for the deviation of point C from its line, but believe that it is connected with a slight difference in the composition of the bottoms and the overhead cuts. These data indicate strongly that as long as the composition in terms of hydrocarbon types is constant, blends made up on the basis of equal moles of solvent per gram of resin will all have the same viscosity even though the molecular weight of the solvent varies considerably.

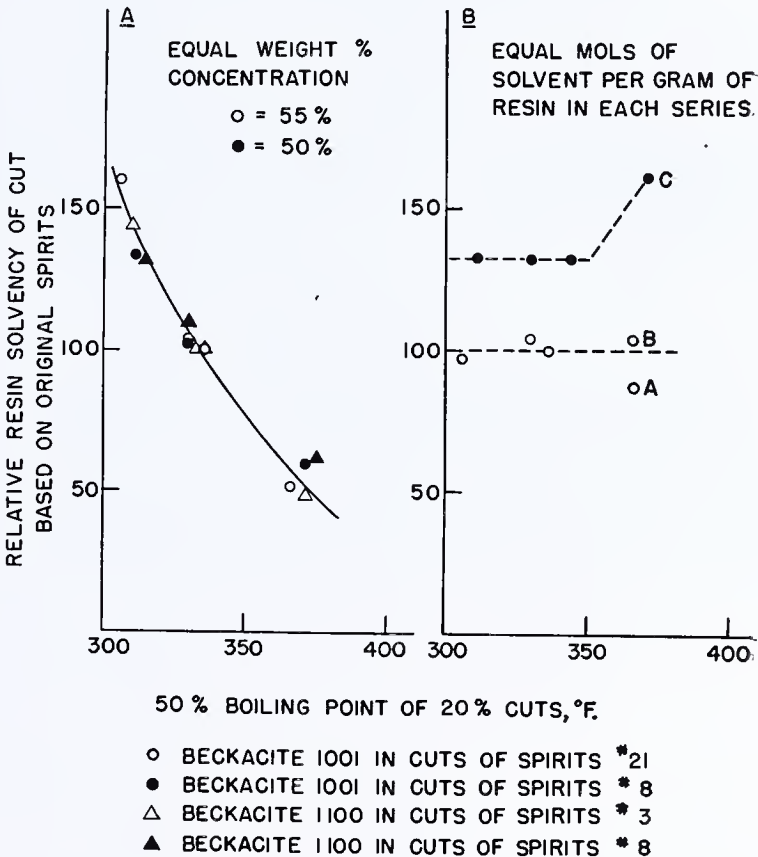


FIGURE 4. RESIN SOLVENCY OF CUTS RELATIVE TO ORIGINAL SPIRITS vs. 50 PER CENT BOILING POINT OF CUTS

The curves in Figure 4, A and B, show that, if blends are made from the cuts of any one spirit on the basis of equal moles of solvent of constant composition per gram of resin, the viscosities of solutions of phenolic resin will be approximately equal—i. e., the solvency on a molar basis is equal, at least over the range for which data have been obtained.

The gain in solvency with decrease in boiling point for any one type of spirit is, therefore, directly related to the gain in the number of molecules per unit volume or weight of the solvent.

Carrying this idea a step further it should follow that with any one type of solvent the number of grams of resin per gram mole of solvent should control the viscosity. To check this idea, Figure 5, in which log viscosity is plotted against grams of resin per gram mole of solvent ( $\times 100$ ), was prepared.

Data are presented for spirits 18 and 21 (which are almost identical with the working standard 2), for spirit 8 which is highly naphthenic, and for 20 per cent cuts of these spirits. It is clear that plotting viscosity against grams of resin per gram mole of solvent ( $\times 100$ ) puts all the data for any one spirit and resin on a single straight line.



TABLE VI. COMPARISON OF FOUR COMMERCIAL SPIRITS

Spirits	Composition Approximately Balanced				Composition Unbalanced			
	2		4		10		11	
50% A. S. T. M. boiling point, ° F.	333		341		339		340	
Approximate composition, volume %:								
Aromatics	30		30		12		15	
Naphthenes	25 to 30		30 to 35		10 to 15		70 to 75	
Paraffins	40 to 45		35 to 40		73 to 78		10 to 15	
	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)	R. S.	R. R. S. (2)
Phenolic (Beckacite 1001)	101	100	92	91	48	47	45	44
Glycerol-rosin (ester gum 6)	134	100	117	87	142	106	62	46
Alkyd (Glyptal 2464)	77	100	75	98	127	110	33	43
Modified rubber (Pliolite)	115	100	105	91			79	69

This would appear to be a valid modification of the well-known approximate relation

$$\frac{\text{Log relative viscosity}}{\text{concentration}} = \text{constant}$$

which is discussed by Staudinger (27, p. 59; 29). (Relative viscosity = viscosity of solution ÷ viscosity of solvent, 28, 29.) The constant in this equation is related to the molecular magnitude of the dispersed material and has been considered (14, 27, 29) as a basis for determining relative molecular weights in homologous series of long-chain compounds.

### Significance of Resin Solvency Test

The resin solvency test, although developed independently, may be considered as a refinement of the viscosity tests of Mantell and Skett (22) and of Ware and Teeters (32). These tests are similar to the resin solvency test in that they involve measurement of the viscosity of a dispersion of resin in a solvent which will completely dissolve the resin. The advantage of reporting in terms of the resin solvency is that the resin solvency values are approximately independent of the

concentration at which the test is made and of temperature. If the viscosity of solutions of a nonchanging resin in the working standard at several concentrations is known, it has been shown (Figure 3) that the viscosity at only one concentration need be determined on a new spirit in order to set up curves of the Ware and Teeters type.

Without discussing in detail the relation of the composition of spirits to their resin solvency, it is of interest to compare two commercial petroleum spirits having a balanced composition, with one rich in naphthenes, and another rich in paraffins. Table VI gives approximate composition data, resin solvency, and relative resin solvency data for such spirit samples.

Spirits 2 and 4, whose compositions are approximately balanced, show relatively little variation in resin solvency, although the higher boiling point of spirit 4 reduces all the resin solvenices somewhat. Spirit 10, which is low in aromatics and naphthenes but rich in paraffins, is very satisfactory for ester gum and Pliolite but very poor for the phenolic type. Spirit 11, which is rich in naphthenes, has low resin solvency for all resins tried.

These data show, definitely, that conclusions concerning the relative solvency of aromatics, paraffins, and naphthenes based on the careful study of the kauri butanol test by Baldeschwieler, Morgan, and Troeller (3, 4) cannot be generalized to apply to a wide variety of materials (18). The data furthermore confirm the statement that one must always keep in mind what is to be solvated when considering "solvency."

The correlation of resin solvency values with the behavior of the solvent in actual manufacturing operations will require the cooperation of the consumer of spirits.

### Summary

There is no definite relation between the kauri butanol solvency of petroleum spirits and the viscosity of cold-cut solutions of resins dispersed in these spirits.

The resin solvency for cold-cut dispersions defined by the equation

$$\text{R. S.} = \frac{\text{kinematic viscosity of solution of X per cent resin in standard spirit 1}}{\text{kinematic viscosity of solution of X per cent resin in spirits under test}} \times 100$$

is approximately independent of the concentration at which the test is made and is approximately independent of the temperature of test.

The resins recommended for test purposes are: (1) Beckacite 1001 (Reichhold Chemical Co.), a straight phenolic resin, which can also represent the modified phenolic class as far as distinguishing between good and poor solvents is concerned; (2) ester gum 6 (American Cyanamid Co.) for the ester gum class of resins.

The relative solvent power of spirits depends upon the type of resin with which the resin solvency is determined.

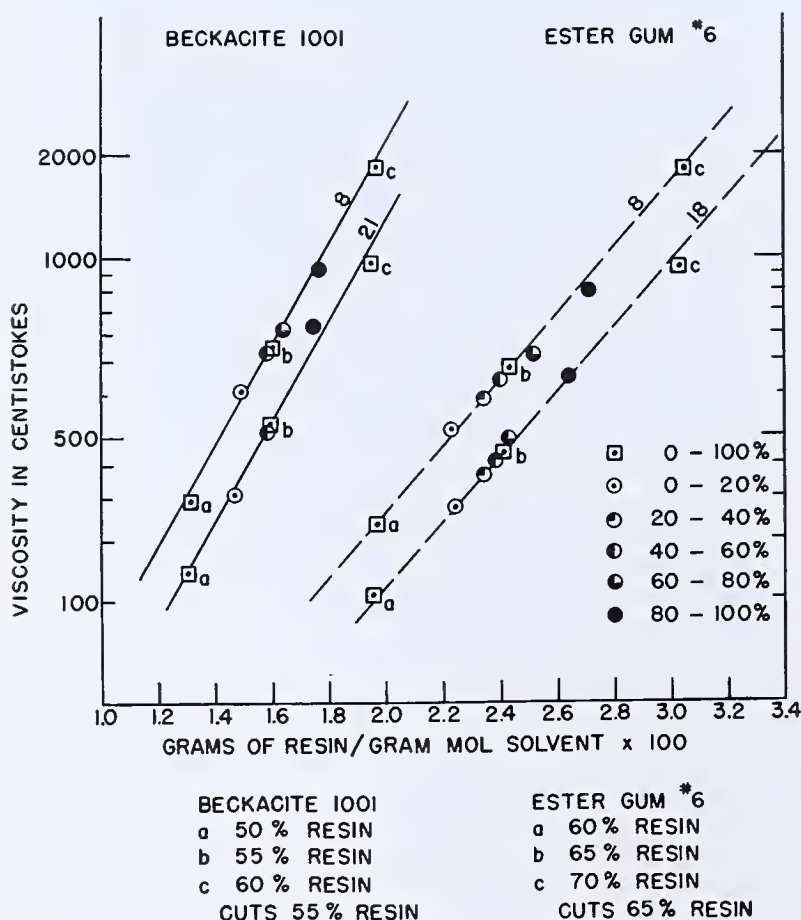


FIGURE 5. VISCOSITY IN CENTISTOKES vs. CONCENTRATION EXPRESSED ON A MOLAR BASIS



Spirits which contain approximately equal proportions of paraffins, naphthenes, and aromatics, however, have good solvency for any of the spirit-soluble resins.

Theoretical background based on the work of McBain, Kraemer, and Staudinger provides a reasonable explanation of the fact that relatively high viscosities are obtained when resins are dispersed in solvents which do not contain enough of the right type of molecule to solvate them completely.

The logarithm of the kinematic viscosity is proportional to the concentration expressed as grams of resin per gram mole of solvent. This is an extension of the generalization of Staudinger, and accounts for the lower viscosity of dispersions prepared with low-boiling cuts of spirits.

The entire study reported is confined to spirits or cuts lying within the boiling range of 300° to 400° F.

A means of standardizing the petroleum spirits used as a working standard is given. The ultimate standard is a mixture of equal volumes of diethylbenzene, decahydronaphthalene, and isooctane.

The resin solvency test is recommended as precise and quantitative, showing relative solvent power of spirits for resins on a cold-cut basis and in the absence of any third component.

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## Vial Holder

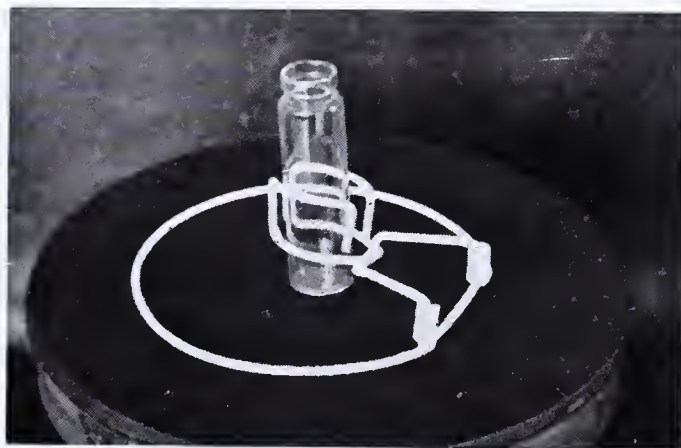
JOHN A. QUENSE AND WILLIAM M. DEHN

University of Washington, Seattle, Wash.

THE vial holder depicted is of great convenience for heating test tubes or vials or filtering into them, as its large base prevents spilling.

The holder is constructed of two pieces of No. 13 W. & M. spring brass wire or No. 16 W. & M. copper-plated steel wire, one piece forming most of the ring, including the two spirals, and the other forming the jaws and the part of the ring connecting the two spirals. The ring may be 3 to 4 inches or more in diameter, the size of wire being increased with the larger diameters.

In filling or filtering into vials or test tubes, the holder frees both hands for manipulation. The jaws may be adjusted to allow any desired portion of a vial to project into a steam bath for heating. When heating on a hot plate, the vial can be raised from the plate to vary the intensity of heating. The holder serves as an individual test tube rack, facilitating the observation of exothermic and other reactions.



VIAL HOLDER



# The Solvency of Petroleum Spirits

## Graphic Determination of Resin Solvency from Boiling Point Density and Refractive Index

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THE experimental determination of resin solvency (3) is rather time-consuming and requires the attention of a skilled operator, if precise results are to be obtained. It has been found that the resin solvency of spirits and cuts of spirits boiling in the range 300° to 400° F. can be derived with considerable accuracy from the 50 per cent boiling point, the density ( $d_{20/4}$ ), and the refractive index ( $n_{20/D}$ ). The solvency thus derived is called the graphic resin solvency (G. R. S.).

Standard resins for each general class are chosen—for example, Beckacite 1001 (Reichhold Chemical Company) for the straight phenolic and modified phenolic classes (2), and ester gum 6 (American Cyanamid Co.) for the ester gum class. A graph is then prepared relating the density and refractive index to the resin solvency for a material of 50 per cent boiling point at 333° F.

If refractivity intercept (5, 7, 8) is plotted against density for a mixture of aromatic, naphthenic, and paraffinic hydro-

carbons, it has been shown (4) that the position of a point on such a graph is definitely related to the proportion of the components in the mixture. In the case of the present work, the solvent power or resin solvency of the spirits for chosen representative resins is needed, and not the composition in terms of hydrocarbon types. By determining the resin solvency of many samples of spirits of widely differing composition, but of known properties, it was found possible to construct Figure 1 which is intended for use with commercial spirits of approximately 300° to 400° F. boiling range. The derivation is a straight-forward empirical method based on properties of samples of commercial spirits and the viscosities of resin solution prepared with these spirits. This graph carries one directly from the density and refractive index to a "normal resin solvency" scale *A* for Beckacite 1001 and *B* for ester gum 6, which equals the resin solvency, provided the A. S. T. M. 50 per cent boiling point (1) of the spirits is 333° F.

The data necessary for the practical construction of this graph are given in Table I.

Points for two petroleum spirits, 2 and 4, of approximately balanced composition, one highly paraffinic petroleum spirit, 10, and one highly naphthenic petroleum spirit, 11, are plotted on the graph. One may say that, approximately at least, increasing resin solvency for Beckacite 1001 indicates an increasing per cent of aromatics, and that decreasing resin solvency for ester gum indicates an increase in the naphthene content.

It is clear that when the 50 per cent boiling point is 333° F.

and the resin solvencies for Beckacite 1001 and for ester gum 6 are specified, the physical properties and approximate composition are also specified.

If the 50 per cent point differs from 333° F., two corrections must be applied to the "normal resin solvency" to obtain the graphic resin solvency. The first is a correction for the effect of variation in boiling point on the physical properties; the second is a correction for the change of molecular weight with change in boiling point which, in a mixture of any given weight per cent or volume per cent concentration, affects the number of moles of solvent per gram of resin.

Using the data for pure compounds tabulated by Ward and Kurtz (7), it was found that the effect of boiling point on the physical property graph would be taken care of by adding a

TABLE I. DATA FOR CONSTRUCTION OF RESIN SOLVENCY GRAPHS

	Phenolic Resins (Beckacite 1001)		Ester Gum Resins (Ester Gum 6)	
	$d_{20/4}$	$n - d/2$	$d_{20/4}$	$n - d/2$
Definitive points for line of 100 resin solvency	0.8300	1.0465	0.8300	1.0503
Interval of line spacing	0.7400	1.0553	0.7400	1.0388
	10 R. S. units = 0.00132 intercept unit		10 R. S. units = 0.00132 intercept unit	

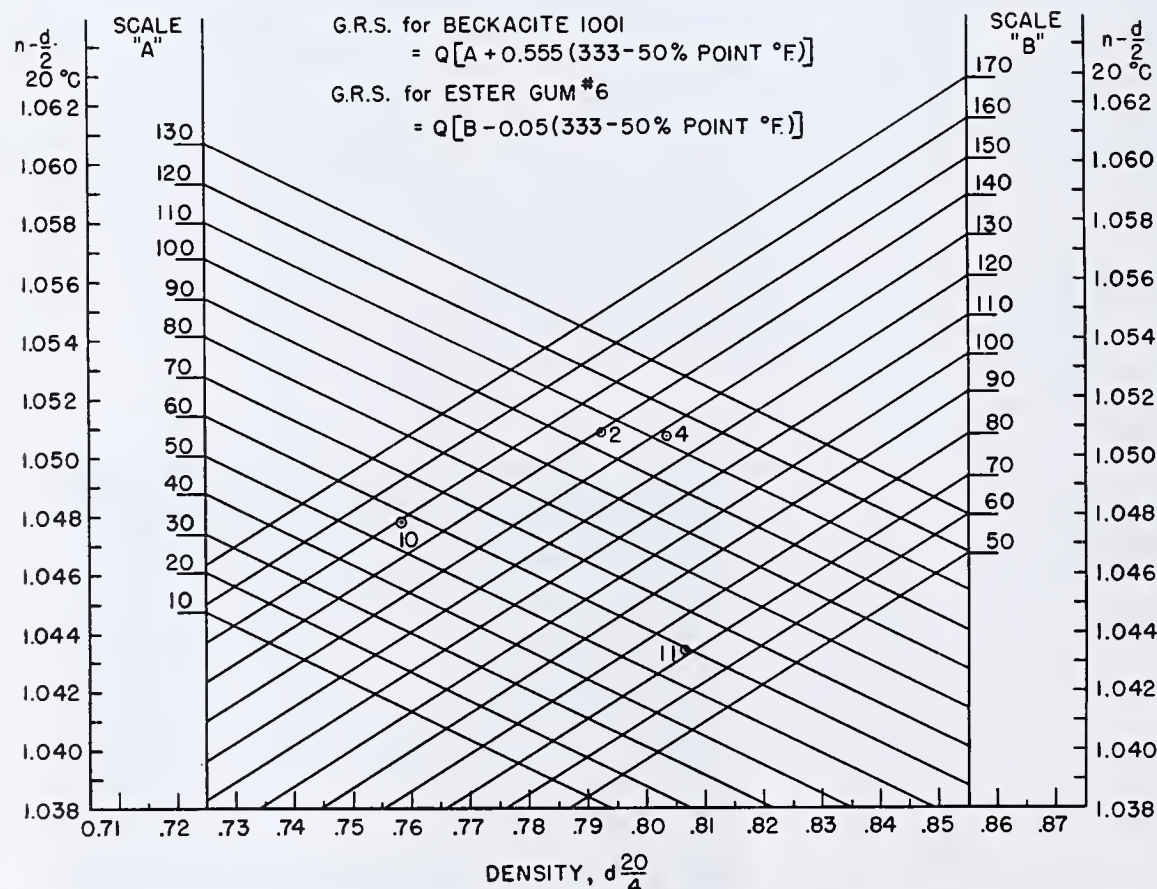


FIGURE 1. GRAPH FOR DETERMINING RESIN SOLVENCY FROM DENSITY, REFRACTIVE INDEX, AND 50 PER CENT BOILING POINT



TABLE II. *Q* FACTOR FOR EFFECT OF MOLECULAR WEIGHT IN CALCULATION OF GRAPHIC RESIN SOLVENCY FOR BECKACITE 1001 AND ESTER GUM 6

Boiling Point above 333° F. ° F.	<i>Q</i>	Boiling Point below 333° F. ° F.	<i>Q</i>
333	1.00	333	1.00
334	0.99	332	1.02
335	0.97	331	1.03
340	0.90	330	1.05
345	0.83	325	1.13
350	0.77	320	1.22
355	0.71	315	1.31
360	0.65	310	1.41
365	0.60	305	1.52
370	0.55	300	1.64
375	0.50		
380	0.46		
385	0.42		
390	0.38		
395	0.34		
400	0.30		

correction, *a*, to the *A* scale of Figure 1, and subtracting a correction, *b*, from the *B* scale of Figure 1 where

$$a = 0.555 (333^\circ \text{ F.} - 50\% \text{ point } ^\circ \text{ F. at 760 mm.})$$

$$b = 0.05 (333^\circ \text{ F.} - 50\% \text{ point } ^\circ \text{ F. at 760 mm.})$$

The 50 per cent point is the volumetric 50 per cent boiling point as observed in the usual A. S. T. M. distillation (1). When determined at sea level, corrections for variation in barometric pressure may usually be neglected.

The correction for variation of molecular weight with boiling point was also worked out using three sets of data as follows: the A. S. T. M. 50 per cent boiling point, the linear relation between log kinematic viscosity and molecular concentration of solvent, and a curve relating 50 per cent boiling point to molecular weight for cuts of spirits (Figure 2). The molecular weights for the spirits curve in this graph were determined cryoscopically in benzene. For the authors' purpose the slope of the curve rather than the absolute value of the molecular weight is of importance. The agreement in regard to slope between the authors' data for cuts of spirits, and the average pure compound data, justifies extrapolating their data for spirits and cuts of spirits.

In regard to the 50 per cent boiling point, consideration was given to the system of Smith and Watson (6) which involves first calculating the volumetric average boiling point, and then correcting this value to another derived boiling point suitable for correlation with certain properties.

The volumetric average boiling points based on the 10, 30, 50, 70, and 90 per cent points for the spirits in Table II of (3) were consistently  $2^\circ \pm 1^\circ \text{ F.}$  higher than the observed A. S. T. M. 50 per cent boiling points.

The mean average boiling point of Smith and Watson, which they found to give a good correlation with molecular weight, leads to a correction of approximately  $-3^\circ \text{ F.}$  from the volumetric average boiling point. Therefore, in the case of spirit samples, the two corrections practically cancel—i. e., the observed 50 per cent point in the A. S. T. M. distillation is practically the same as the mean average boiling point. Therefore, the observed A. S. T. M. 50 per cent point was used without correction.

The authors' correction for effect of boiling point on molecular weight and consequently on viscosity of the dispersions takes the form of a multiplication factor designated as *Q*. The derivation of these *Q* factors is perhaps best illustrated by a definite example.

Consider a spirits of 360° F. (182.2° C.) 50 per cent boiling point (A. S. T. M.) which is to be referred to a standard 50 per cent boiling point of 333° F. (167.2° C.) A. S. T. M. Figure 2 shows that the molecular weights corresponding to these boiling points are 140.5 and 130, respectively. The

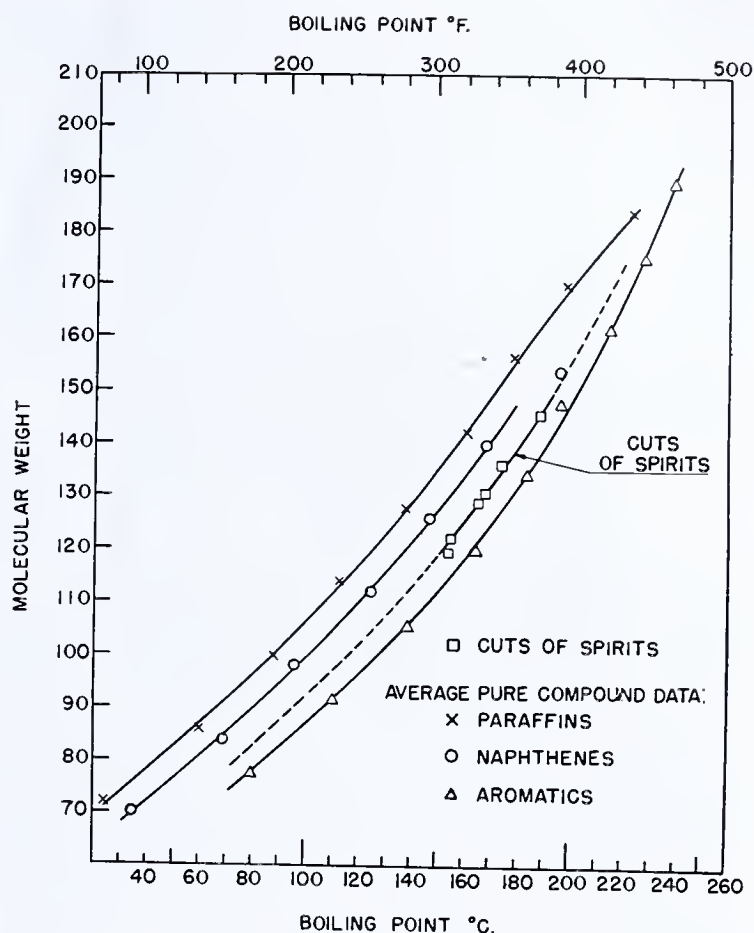


FIGURE 2. MOLECULAR WEIGHT vs. BOILING POINT

molecular concentration of solvent expressed as grams of resin divided by 100 times the gram moles of solvent is given by the following calculation:

Boiling Point of Solvent ° F.	55% Weight, Beckacite 1001	65% Weight, Ester Gum 6
333	$55 \div 100 \frac{45}{130} = 1.59$	$65 \div 100 \frac{35}{130} = 2.41$
360	$55 \div 100 \frac{45}{140.5} = 1.72$	$65 \div 100 \frac{35}{140.5} = 2.62$

The viscosities corresponding to these molar concentrations of solvent are obtained from Figure 5 (3) as follows:

Boiling Point of Solvent ° F.	55% Weight, Beckacite 1001 Centistokes	65% Weight, Ester Gum 6 Centistokes
333	325	269
360	500	422
Ratio of viscosities, <i>Q</i>	0.65	0.64

The viscosity of the solution made up with the high- or low-boiling solvent divided into the viscosity of the solution made up with the solvent having a 50 per cent point (A. S. T. M.) at 333° F., is the *Q* factor. As shown above, the *Q* factors calculated from the data of solutions of Beckacite 1001 and solutions of ester gum 6 check within about 1 per cent. This is so because the per cent change in grams of resin per gram mole of solvent for any given increment of viscosity is practically the same. It is not possible at present to generalize further, because there are indications that different scales of *Q* factors may be needed for resins of widely differing molecular complexity such as Pliolite.

Table II contains the *Q* factors calculated for this work. For intermediate boiling points, the factors may be obtained by interpolation.



TABLE III. COMPARISON OF GRAPHIC AND EXPERIMENTAL RESIN SOLVENCY

Solvent	50% A. S. T. M.				Beckacite 1001				Ester Gum			
	Boiling Point ° F.	Experimental	Graphic	Difference	Experimental	Graphic	Difference		Experimental	Graphic	Difference	
12	324	118	122	+ 4	...	...	..		...	...	..	
13	328	115	116	+ 1	...	...	..		...	...	..	
14	331	109	106	- 3	...	...	..		...	...	..	
15	329	108	109	+ 1	...	...	..		...	...	..	
16	332	105	100	- 5	...	...	- 2		...	...	..	
18	331	104	103	- 1	137	135	..		...	...	..	
19	333	101	101	0	...	...	..		...	...	..	
20	332	101	103	+ 2	...	...	..		...	...	..	
2	333	101	105	+ 4	134	139	+ 5		...	...	..	
21	336	98	94	- 4	...	...	..		...	...	..	
22	330	95	97	+ 2	...	...	..		...	...	..	
23	336	93	93	0	...	...	..		...	...	..	
3	336	93	95	+ 2	123	125	+ 2		...	...	..	
24	331	91	90	- 1	...	...	..		...	...	..	
25	342	86	81	- 5	...	...	..		...	...	..	
4	341	92	96	+ 4	117	114	- 3		...	...	..	
5	333	87	90	+ 3	...	...	..		...	...	..	
6	336	81	85	+ 4	102	98	- 4		...	...	..	
28	333	68	55	-13	55	32	-23		...	...	..	
29	333	64	68	+ 4	106	111	+ 5		...	...	..	
7	338	66	63	- 3	109	108	- 1		...	...	..	
30	338	63	62	- 1	111	113	+ 2		...	...	..	
8	336	58	53	- 5	80	73	- 7		...	...	..	
9	340	55	53	- 2	121	117	- 4		...	...	..	
10	339	48	50	+ 2	142	136	- 6		...	...	..	
31	347	46	45	- 1	99	98	- 1		...	...	..	
11	340	45	50	+ 5	62	65	+ 3		...	...	..	
32	387	30	24	- 6	56	45	-11		...	...	..	
27	331	30	39	+ 9	...	...	..		...	...	..	

Solvent	50% A. S. T. M. Boiling Point ° F.	Experimental	Graphic	Difference	Experimental	Graphic	Difference
21							
0- 20%	306	157	166	+ 9	...	...	..
40- 60%	330	102	107	+ 5	...	...	..
80-100%	366	51	46	- 5	...	...	..
8							
0- 20%	311	73	86	+13	...	...	..
40- 60%	330	56	64	+ 8	...	...	..
60- 80%	344	50	61	+11	...	...	..
80-100%	371	32	32	0	...	...	..
18							
0- 20%	308	...	...	..	196	199	+ 3
20- 40%	321	...	...	..	160	157	- 3
40- 60%	326	...	...	..	143	147	+ 4
60- 80%	336	...	...	..	125	123	- 2
80-100%	361	...	...	..	82	78	- 4
8							
0- 20%	306	...	...	..	117	135	+18
20- 40%	321	...	...	..	97	103	+ 6
40- 60%	331	...	...	..	85	86	+ 1
60- 80%	345	...	...	..	68	71	+ 3
80-100%	373	...	...	..	47	39	- 8
				No. of Samples			
+ deviation				19			
- deviation				14			
No deviation				3			
Av.					4.1		
						5.2	

The complete graphic resin solvency equation for Beckacite 1001 is

G. R. S. = Q [A + 0.555 (333° F. - 50% boiling point ° F. at 760 mm.)]

For ester gum 6 it is

G. R. S. = Q [B - 0.05 (333° F. - 50% boiling point ° F. at 760 mm.)]

In regard to the precision of data required, it is desirable that the density should be accurate within ±0.0005 and the refractive index should be accurate within ±0.0002. A curve for correcting specific gravity 60/60 to d 20/4 for petroleum products has been published (7); therefore, densities of sufficient accuracy can be obtained by the careful use of large A. P. I. hydrometers and this curve. Pycnometer densities are, however, somewhat more reliable. Any modern Abbe refractometer should give refractive index measurements of sufficient accuracy.

For a more complete discussion of density and refractive index determination, one may refer to Ward, Kurtz, and Fulweiler (8).

As an example of the use of Figure 1, consider solvent 10 and the 0 to 20 per cent cut of spirit 18.

SOLVENT 10

50% A. S. T. M. boiling point, ° F.	= 339
Density (d 20/4)	= 0.7582
Refractive index (n 20/D)	= 1.4268
Refractivity intercept (n - d/2)	= 1.0477

The resin solvency for Beckacite 1001 is derived using the A scale of Figure 1. The A scale value corresponding to the given properties is 57. The a correction for 339° F. is a = 0.555 × (333 - 339) or -3.3. Therefore, A corrected = 54. For 339° F. 50 per cent boiling point Q from Table II is 0.92. The graphic resin solvency = 54 × 0.92 = 50. The determined resin solvency was 48; therefore, the graphic resin solvency is in error by only +2 unit in this case.

0 TO 20% CUT OF SOLVENT 18

50% A. S. T. M. boiling point, ° F.	= 308
Density (d 20/4)	= 0.7891
Refractive index (n 20/D)	= 1.4447
Refractivity intercept (n - d/2)	= 1.0502

The B scale value from Figure 1 corresponding to the above density and intercept is 138. The b correction for 308 is b =

0.05 (333 - 308) = -1.25. This correction must be subtracted; therefore, B corrected is 137. For 308 the Q factor (Table II) is 1.45. The graphic resin solvency = 137 × 1.45 = 199. The determined resin solvency with ester gum 6 is 196; therefore, the graphic resin solvency is in error by only +3 units.

Table III shows that in general the graphic resin solvency agrees with the experimental within ±5 units. Since these graphs depend on the average properties of the compounds in natural spirits, they cannot be expected to apply to synthetic blends of pure compounds.

Summary

Graphs have been developed so that the resin solvency of spirits for phenolic resins (Beckacite 1001, Reichhold Chemical Company) and ester gum resins (ester gum 6, American Cyanamid Company) can be determined from the A. S. T. M. 50 per cent boiling point, the density (d 20/4) and the refractive index (n 20/D).

Conversely, specifications of boiling point and resin solvency for ester gum 6 and Beckacite 1001, automatically specify the physical properties and approximate composition of the solvent.

These graphs give results agreeing with the experimental resin solvency within ±5 units, which is considered satisfactory.

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# Colorimetric Method for Determination of Barium

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ALTHOUGH barium is commonly determined gravimetrically as the sulfate or chromate, the ignition of the sulfate and the careful drying of the chromate require considerable time. In the analysis of barium samples of relatively low concentration a colorimetric method should prove valuable as a time-saver. The tannic acid method recommended by Ammer and Schmitz (1) for colorimetrically determining barium is not very satisfactory, since the color obtained is transitory and lasts only from 3 to 5 minutes. Likewise, the method proposed by Friedrich and Rapoport (5), making use of sodium rhodizionate and gelatin, yields colored solutions that are not stable in the presence of light.

Solid barium chromate is sufficiently stable and uniform in composition to be used as a gravimetric method (2, 14) and when dissolved yields solutions that have been satisfactorily used as a basis for a volumetric method (13). It was therefore believed that the solution could well be used for colorimetrically estimating small amounts of barium.

The use of chromate solutions for colorimetrically determining small quantities of chromium is well known. The results are obtained rapidly and are recognized as accurate. The work of Horn (6) showed definitely that the maximum color sensitivity of chromate solutions lies between 0.004 and 0.008 *N*. Furthermore, Dehn (3) in his extensive studies on solutions of chromic acid, dichromates, and chromates states that below 0.01 per cent (calculated as  $\text{H}_2\text{CrO}_4$ ) "identical shades of yellow are obtained." Inasmuch as the more concentrated solutions are tinged with red it was decided to work with concentrations of barium that would yield chromate solutions comparable to those recommended by both Dehn and Horn.

With these considerations in mind the following work was undertaken and the results obtained were sufficiently accurate and reproducible to warrant using the method for the quantitative determination of barium.

Inasmuch as it is the authors' intention to use the method for work, in this laboratory, on relatively simple solutions, their primary aim was to determine whether or not consistently accurate results could be obtained by this method and if so, the optimum conditions. Since the method merely involves precipitating barium as the chromate, dissolving the precipitate, and using the resultant solution for colorimetric comparison, there was no reason to believe that any trouble would be encountered, inasmuch as each step had proved feasible in other procedures. The data obtained confirmed this belief.

## Apparatus

The work on the percentage absorption of the barium chromate solutions was carried out with a Lange, compensating type, photoelectric cell colorimeter. For consistent results it was found necessary to use as a light source the 6-volt bulb provided with the instrument in conjunction with two 6-volt storage batteries, connected in series and at full charge. Before taking readings the light was turned on and left burning for 30 minutes. No attempt to measure the constancy of voltage or current was made, since it is the consensus of opinion (8) that the photocell itself may be considered as a much more sensitive instrument for such measurements than an external voltmeter or ammeter. Schott's glass filters, which were also provided with the instrument, were used.

For the actual analyses a Klett colorimeter, provided with both 50- and 100-mm. cups, was used. The deeper cups proved to be

of little value since, when enough color for comparison was obtained, the more shallow cups proved deep enough. No work was done with Nessler tubes, since a matched set was not available.

The solutions used were prepared from analytical reagent grade chemicals without further purification. The traces of impurities present (detected spectroscopically) were insufficient to have any bearing on the results obtained.

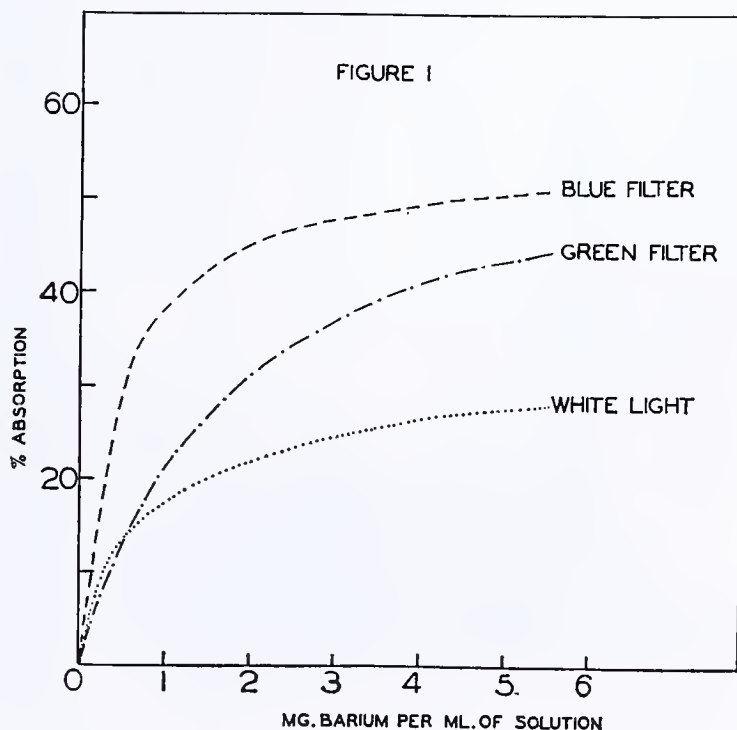
## Procedure

The procedure was that followed in the preparation of both the standard and sample solutions. It is also the method to be followed for all samples after their solution has been effected. It is analogous to that recommended by Scott (10) for the gravimetric and volumetric methods.

To the neutral solution, containing barium, are added 3 drops of glacial acetic acid followed by 10 ml. of 30 per cent ammonium acetate solution. The solution is then heated to boiling and a slight excess of 10 per cent ammonium chromate added dropwise with vigorous stirring. After 30 minutes' digestion the supernatant liquor is decanted through a sintered-glass crucible. The precipitate is then thoroughly washed with hot water (12), dissolved in 10 ml. of cold hydrochloric acid (1 to 1), and diluted to 100 ml. The resultant solution is used for colorimetric comparison.

## Data

The barium titer of the chloride solution used in the preparation of the standards and samples studied was determined gravimetrically both as the sulfate and chromate. From the absorption data obtained (Figure 1) it appears as though a blue filter should tend to greater accuracy in more dilute solutions while a green filter should increase the accuracy in the more concentrated solutions. Furthermore, the indications were that with white light the highest accuracy would be with solutions containing less than 1.5 mg. of barium per milliliter of solution. This range is slightly higher than





that indicated by Dehn and Horn. Unfortunately, no filters were available for use with the Klett, so that all the visual work had to be carried out with white light. It is intended, however, to determine the usefulness of the above-mentioned filters in conjunction with further work now being carried on.

TABLE I. DETERMINATION OF BARIUM

(Using standards containing the same amounts of barium)

Barium Present Standard Mg./ml.	Sample	Colorimeter Standard	Readings Sample <sup>a</sup>	Barium Found Mg./ml.	Error %
0.02808	0.02808	75.0	78.8 <sup>b</sup>	0.02683	-5.00
0.2808	0.2808	15.0	14.99	0.2810	+0.07
	0.2808	30.0	30.02	0.2806	-0.09
0.5616	0.5616	15.0	15.02	0.5608	-0.13
	0.5616	30.0	30.02	0.5612	-0.08
0.8424	0.8424	10.0	10.01	0.8416	-0.10
	0.8424	20.0	20.03 <sup>c</sup>	0.8412	-0.14
1.1232	1.1232	7.5	7.51	1.1217	-0.13
	1.1232	15.0	15.00	1.1232	0.00
1.404	1.404	7.5	7.50	1.404	0.00
	1.404	15.0	15.09	1.396	-0.57
2.808	2.808	7.5	7.51	2.804	-0.14
	2.808	15.0	15.06	2.797	-0.39
5.616	5.616	7.5	7.56	5.571	-0.80
	5.616	15.0	15.13	5.568	-0.85

<sup>a</sup> Average of at least two determinations, each being the average of five readings.

<sup>b</sup> Extremely difficult to match.

<sup>c</sup> Reddish tinge appears.

In Table I are shown the results obtained by comparing various solutions against standards made up simultaneously with the samples and having the same concentration of barium. The most consistent and reproducible results were obtained when solutions containing between 0.3 and 1.0 mg. of barium per milliliter were matched. The colorimeter readings were easily obtained and reproducible within this range. Although it is possible, with practice, to obtain favorable results with more concentrated solutions, measurements must be made through more shallow depths. Extreme care is necessary and the probable error in reading the instrument plays an important part in the determination. The color formed is too intense to permit ready matching at convenient heights of solution. Solutions containing less than 0.2 mg. of barium per milliliter of solution are insufficiently colored for use.

TABLE II. DETERMINATION OF BARIUM

(Using standards containing different amounts of barium)

Barium Present Standard Mg./ml.	Sample	Colorimeter Standard	Readings Sample	Barium Found Mg./ml.	Error %
0.2808	0.02808	3.5	39.3	0.02501	-10.93
	0.5616	30.0	14.98	0.5624	+0.14
	0.8424	15.0	4.96	0.8491	+0.80
0.5616	0.2808	15.0	30.02	0.2806	-0.07
	0.8424	15.0	9.96	0.8458	+0.40
	1.1232	15.0	7.55	1.1158	-0.66
	1.404	15.0	6.00	1.404	0.00
0.8424	0.2808	10.0	30.12	0.2797	-0.39
	0.5616	10.0	15.04	0.5601	-0.27
	1.1232	10.0	7.55	1.1158	-0.66
	1.404	10.0	6.02	1.399	-0.36
1.1232	0.5616	7.5	14.92	0.5646	+0.53
	0.8424	7.5	9.96	0.8458	+0.40
	1.404	7.5	5.99	1.406	+0.14
	2.808	7.5	2.99	2.817	+0.32
1.404	0.8424	7.5	12.30	0.8561	+1.62
	1.1232	7.5	9.44	1.1155	-0.69
	2.808	15.0	7.48	2.815	+0.25
	5.616	15.0	3.80	5.542	-1.31
2.808	0.8424	7.5	24.78	0.8499	+0.89
	1.1232	7.5	18.86	1.1167	-0.58
	1.404	7.5	15.42	1.366	-2.71
	5.616	7.5	3.56	5.916	+5.34
5.616	1.404	5.0	19.86	1.414	+0.71
	2.808	5.0	9.80	2.865	+2.03

The results secured by comparing the samples against solutions with different barium content showed (Table II) that consistent results are again obtained within the above-mentioned limits. These limits may be extended—again if extreme care is used in matching. In general, results ob-

tained by the use of standards similar in strength to the samples are slightly more consistent.

From these data it is evident that the colorimetric method is suitable, particularly within the concentration limits mentioned and preferably with the use of standards essentially similar in strength to the samples. Analysis of a fluorspar sample obtained from the National Bureau of Standards yielded 0.06, 0.06, and 0.09 per cent of barium oxide (average recommended by the bureau was 0.07 per cent). The fluorspar was put into solution by the recommended method (supplied on the certificate provided with the sample), the lead removed electrolytically, and the aforementioned procedure followed.

### Interfering Ions

Inasmuch as in future work one or more of the following cations may be present with the barium, it was thought advisable to investigate their effect upon the method. Barium chromate was precipitated in the presence (individually) of equivalent amounts of the chlorides of sodium, potassium, calcium, magnesium, and strontium. All but strontium had no effect upon the determination of barium. As was expected, strontium caused high results.

TABLE III. EFFECT OF STRONTIUM

(2 mg. of strontium per ml. of solution in a total volume of 100 ml. previous to precipitation)

Barium Calcd. Mg./ml.	Barium Found Mg./ml.	Deviation %
0.5578 <sup>a</sup>	0.7163	+28.42
0.5578 <sup>b</sup>	0.6140	+10.07
0.5578 <sup>c</sup>	0.5523	-0.29

<sup>a</sup> Single precipitation.

<sup>b</sup> Double precipitation with large excess of ammonium chromate.

<sup>c</sup> Double precipitation without addition of excess ammonium chromate.

The procedure recommended for the separation of barium and strontium as chromates by Skrabal and Neustadt (11) was found to yield a satisfactory separation with as high a ratio of strontium to barium in solution as 4 to 1. Their method consists in dissolving the initial impure chromate precipitate in nitric acid, neutralizing the resultant solution with ammonia water, boiling, and adding ammonium acetate drop by drop. This double precipitation without addition of further ammonium dichromate solution yielded final solutions singularly free from strontium. Although the method of Fresenius (4) is suitable in the presence of smaller amounts of strontium, it is not satisfactory when this ion is present in large excess. Precipitation as recommended by Robin (9) from a solution rich in ammonium chloride did not yield consistent results. Although the method of Kahan (?) seems suitable, no advantage over that of Skrabal and Neustadt was apparent, while the 3-hour wait she recommends seems a needless waste of time. The data summarized in Table III represent the average of at least four determinations for each method tried.

Varying the amount of acid used for effecting solution of the precipitate had no effect upon the color produced. Successive solutions were prepared containing equal amounts of barium chromate dissolved in 10 ml. of 1 to 1 nitric acid and in 10, 20, 30, and 40 ml. of 1 to 1 hydrochloric acid. No difference in color could be detected.

### Summary

Barium may be rapidly determined by precipitating as the chromate, dissolving in hydrochloric or nitric acid, and comparing the resultant solution with a colorimetric standard.

In analyzing a solid sample containing barium a sufficient weight of sample should be taken to yield a final solution (for



comparison) containing from 0.2 to 1 mg. of barium per milliliter of solution. The use of green and blue filters may extend these limits. For the lower concentrations, heights of 30 mm. in the colorimeter yield most consistent results, while for the higher concentrations heights of 15 and 20 mm. are recommended.

The presence of sodium, potassium, calcium, and magnesium ions in equivalent amounts does not affect the determination of barium.

The concentration of acid used to effect solution is not critical.

The presence of strontium ion leads to erroneously high results. Its effect may be obviated, as in the gravimetric method, by careful double precipitation.

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## Permanganate Oxidation Index as a Criterion of Coal Rank

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IN A previous paper (6) the senior author discussed the results of a study of the oxygen-absorbing properties of a series of coals ranging from the North Dakota lignites to the Pennsylvania anthracites in which the Heathcoat-Francis (3, 5) method employing a standard solution of potassium permanganate was used. It was shown that when these oxygen values, designated as permanganate numbers, were

plotted in bar graph form in descending series an excellent correlation was obtained with a series of coals arranged in a generally accepted ascending order of rank—i. e., high permanganate numbers corresponded with low-rank coal. In the words of Francis (2), "It appears to be a very promising method for determining the rank of a coal."

The present paper reports progress of this investigation

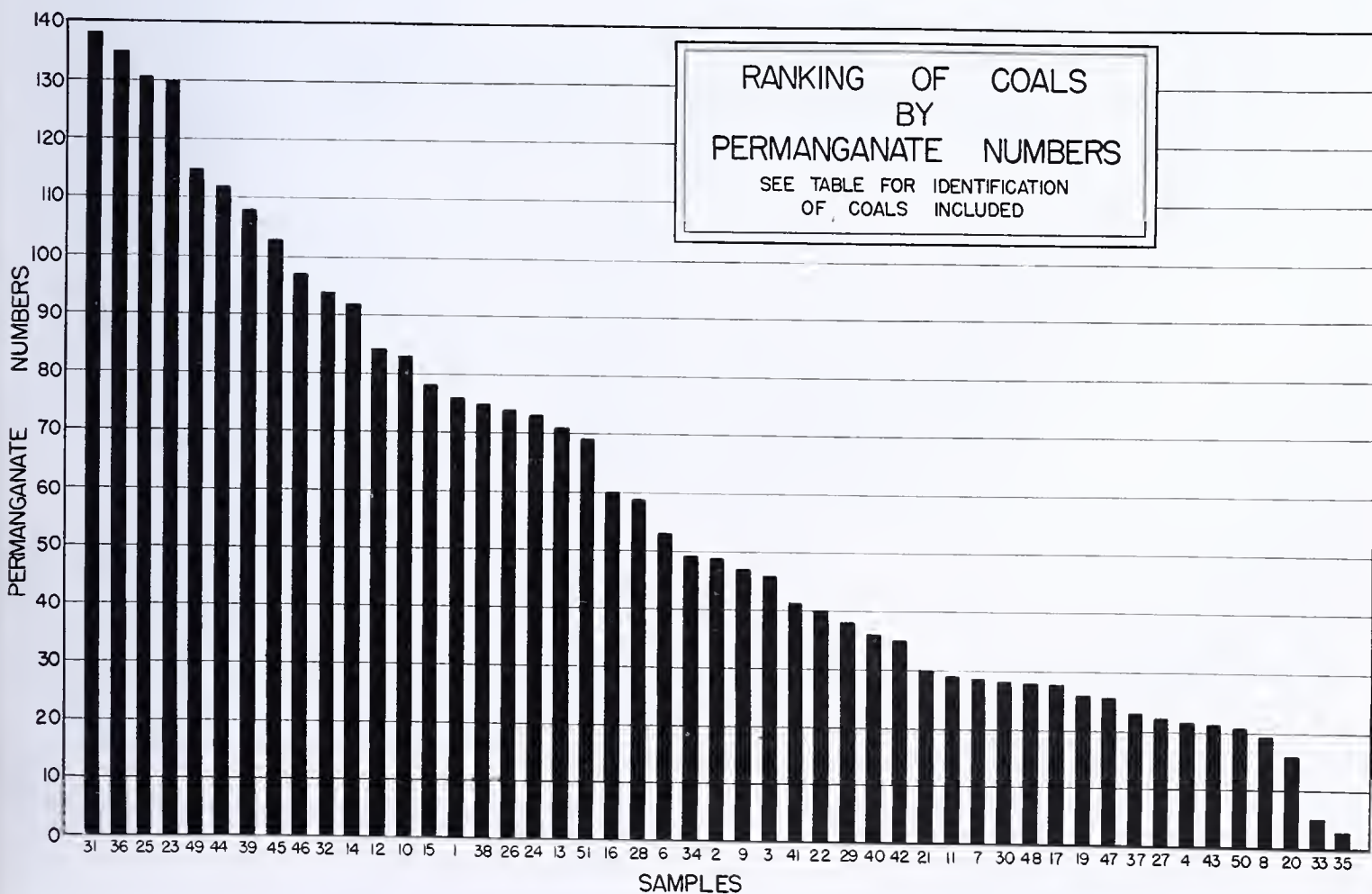


FIGURE 1



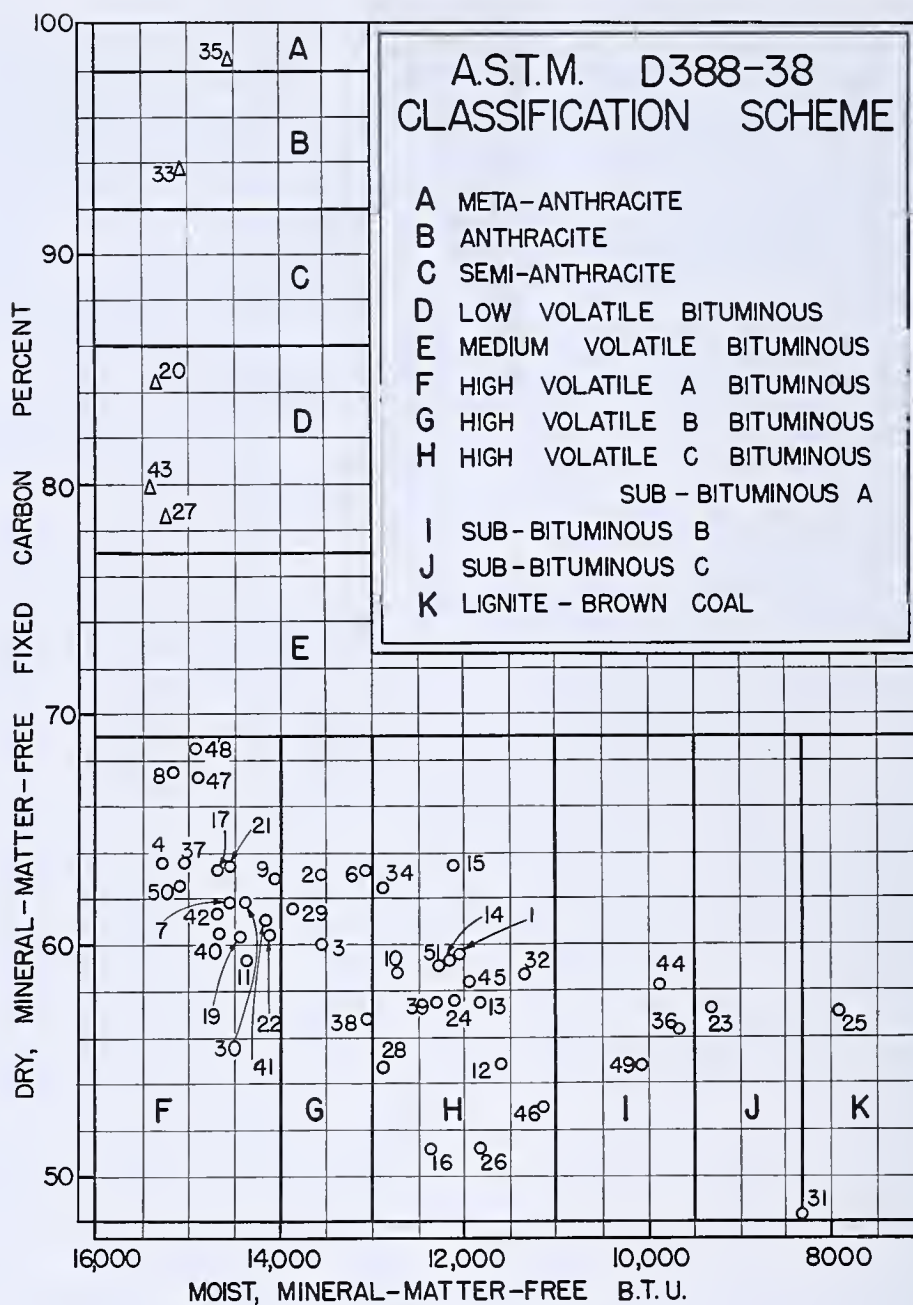


FIGURE 2

along three lines: an improvement of the method whereby greater accuracy and precision of the chemical work are obtained; the inclusion of a greater number and variety of coals studied; and a correlation of the permanganate curve with the curve of the same coals arranged according to A. S.

T. M. specifications D388-38 (1), prepared by the Sectional Committee on Classification of Coals.

### Essentials of the Method

**PARTICLE SIZE.** Coal of 60 × 100 mesh size was selected for this work, for that fraction gave the most consistent final results.

**PYRIDINE EXTRACTION.** About 8 grams of the sized coal were extracted with pyridine for 8 hours in a Soxhlet apparatus.

A more rapid extraction is obtained by first bringing the coal in contact with pyridine at about 60° C. for 30 minutes (to swell the coal to avoid later packing in the extraction thimble) before transferring to the thimble in the Soxhlet apparatus.

**WASHING.** The freshly extracted sample was removed and washed three successive times with acetone.

**DRYING.** The solvent acetone was removed by drying the coal for 6 hours at room temperature in a desiccator under high vacuum to inhibit oxidation of the coal.

**PERMANGANATE DETERMINATION.** One-half gram of the extracted coal was transferred to a 500-ml. flask containing 50 ml. of boiling 1 N sodium hydroxide. The flask was carefully agitated while the coal was being wetted. The length of this contact period influences the final results, but experimental investigation shows that 5 minutes is the optimum time necessary to yield consistent results. Two hundred milliliters of 1 N potassium permanganate solution were heated almost to boiling and transferred completely to the flask containing the extracted coal.

The mixture was gently boiled on a hot plate, in a flask fitted with a stirring device, and with a reflux condenser to prevent water loss. The reaction was permitted to proceed 1 hour from

the time of the permanganate addition.

The contents were then cooled with direct addition of about 200 grams of ice to check the reaction. The mixture was filtered through asbestos and the combined filtrate and washings were diluted to 1000 ml. and titrated into 25-ml. portions of standard 0.1 N oxalic acid. The permanganate number is calculated as the milliliter

volume of 1.0 N potassium permanganate solution reduced by the 0.5 gram of coal under the conditions specified.

The most important of the modifications adopted was the substitution of acetone for hydrochloric acid and water as the washing fluid and the use of the vacuum desiccator at room temperature as a means of drying instead of the air oven at 105° C. By so doing an appreciable error due to slow oxidation during this drying period is avoided, especially important in the case of low-rank coals.

### Discussion

A series of 49 samples covering the greatest practicable range of coals was used in the study. They are listed and briefly described in Table I.

The new series of permanganate numbers is plotted in Figure 1, the numerals under each bar corresponding to the numbers of Table I. A study of the reproducibility of check determinations showed that the mean deviation can easily be kept below 1.6 per cent. Considering the wide range of this constant in different coals—from 140 to 2—this is highly satisfactory agreement and we may conclude that the method is adequately precise.

In Figure 2 are charted the locations of the coals studied according to A. S. T. M. Designation 388-38 (1) wherein areas A, B, C, D, E, and F include those with dry, mineral-matter-



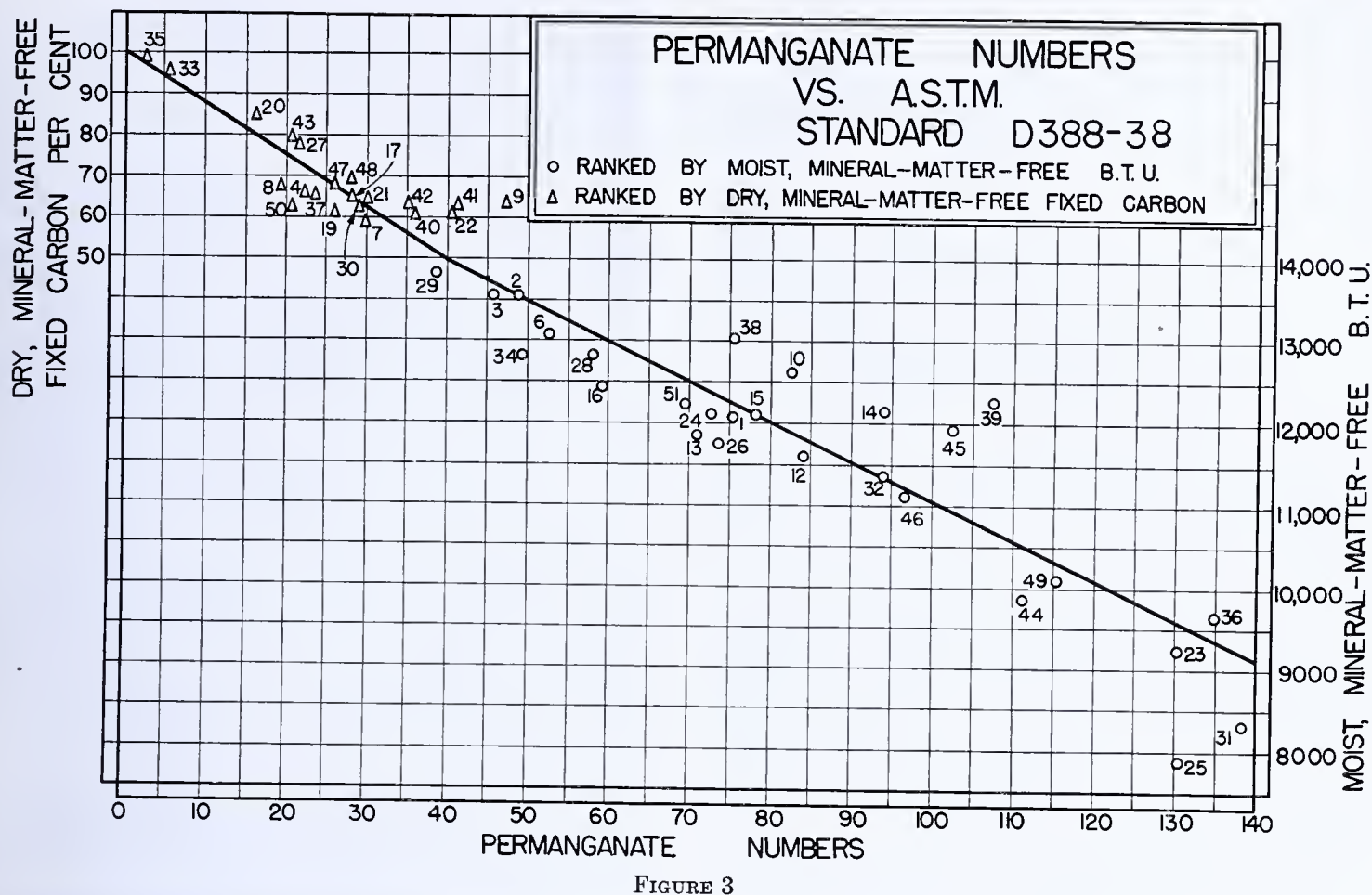


TABLE I. PERMANGANATE NUMBERS OF COALS

Sample No.	State	County	Seam <sup>a</sup>	Mine	Permanganate Number
31	Texas	Milam	Lignite	Sandow	138
36	Colo.	Jackson	Coalmont		135
25	N. D.	Divide	Noonan	Baukol-Noonan	130
23	Mont.	Blaine	Lignite	Milk River	130
49	Wyo.	Sheridan	Monarch	Monarch No. 45	115
44	Colo.	Weld	Laramie	Baum	112
39	Wyo.	Sweetwater	No. 1		108
45	Iowa	Polk	No. 3	Norwood-White No. 8	103
46	Iowa	Webster	No. 3		97
32	Iowa	Dallas	No. 3	Waukee No. 1	94
14	Ill.	Christian	No. 6	Langley No. 9	93
12	Iowa	Appanoose	Mystic	Sunshine No. 3	85
10	Ill.	Randolph	No. 6	Moffat No. 2	83
15	Ind.	Sullivan	No. 6	Friar Tuck	77
1	Ill.	Madison	No. 6	Thermal	75
38	Colo.	Gunnison	Mesaverde No. 1	Bulkley No. 2	75
26	Iowa	Monroe	No. 3	Graham No. 2	75
24	Ill.	Will	No. 2		73
13	Iowa	Mahaska	No. 3	Atlas	72
51	Ill.	Fulton	No. 6	Middle Grove	69
16	Ill.	Henry	No. 2	Atkinson	60
28	Ind.	Vigo	No. 5	Chieftain No. 20	59
6	Ill.	Franklin	No. 6	Ziegler No. 1	54
34	Ky.	Muhlenberg	Green River	Green River	49
2	Ill.	Saline	No. 5	Harco No. 47	49
9	Ky.	Perry	Hazard No. 7	Glomawr No. 5	47
3	Ky.	Hopkins	No. 6	Daylight No. 6	48
41	Va.	Lee	No. 10-Pardee	Bonny Blue	41
22	Ky.	Whitley	Jellico	Dixie Gem	40
29	Okla.	Okmulgee	Henryetta	Atlas No. 2	38
40	Va.	Lee	High Splint	Mayflower	36
42	Ky.	Harlan	Harlan	Crown	35
21	Ky.	Harlan	No. 5	Greatheart No. 31	30
11	Ky.	Union	No. 9		29
7	Ky.	Floyd	Elkhorn No. 1	Glo No. 1	29
30	Penna.	Butler	U. Kittanning		38
48	Ala.	Walker	Mary Lee	Gamma	28
17	Tenn.	Claiborne	Jellico	Eagan	29
19	Ky.	Perry	Hazard No. 4	Palmer	27
47	Tenn.	Grundey	Sewanee		26
37	Ky.	Pike	Alma		23
27	Penna.	Clearfield	L. Kittanning	Penneneec	23
4	W. Va.	Raleigh	Dorothy	Montcoal No. 1	22
43	Penna.	Tioga	Bloss	Morris Run No. 1	22
50	Ala.	Jefferson	Black Creek	Bradford	22
8	Va.	Russell	Red Ash	Candlewax	19
20	W. Va.	McDowell	Pocahontas No. 3	Upland No. 1	16
33	Penna.	Schuylkill	Skidmore		5
35	Penna.	Schuylkill	Primrose	Mahanoy City	3

<sup>a</sup> Seam numbering follows authority of Keystone Manual (4).

free fixed carbon percentages above 69 per cent and G, H, I, J, and K those with moist mineral-matter-free thermal values less than 14,000 B. t. u. Acting on the assumption that if two independent systems of classification are both fundamentally sound they should bear some definite relation to each other, the authors combined Figures 1 and 2 in Figure 3 by plotting permanganate numbers against moist mineral-matter-free thermal values up to 14,000 B. t. u. (providing fixed carbon is less than 69 per cent) and beyond that, against dry mineral-matter-free fixed carbon. In general the curve describes a straight line; in spite of discrepancies it is a striking correlation and indicates that the permanganate number is a significant function of the chemical age of a coal and therefore of its rank.

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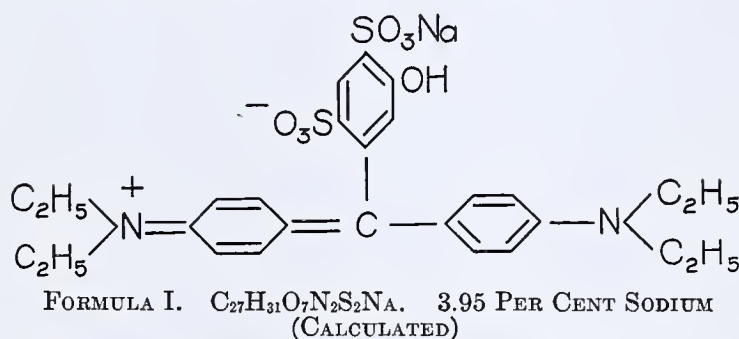
# Patent Blue V as a pH and Redox Indicator

JOHN H. YOE AND GEORGE R. BOYD, JR., University of Virginia, Charlottesville, Va.

PATENT blue V acts as an indicator of hydrogen-ion concentration and in oxidation-reduction titrations. It forms bright stable colors over the pH range 0.8 to 3.0 and also undergoes a sharp color change at the equivalence point in the titration of ferrous ions with ceric sulfate. As no reference to its use as an indicator was found in the literature, an investigation of these two types of indicator action seemed desirable.

Patent blue V is a dye of the triphenylmethane series to which Erdmann (4) assigned the formula  $C_{27}H_{31}O_7N_2S_2Na$ . As commercially prepared, it may be the sodium, calcium, or magnesium salt, plus certain impurities, chiefly inorganic salts.

Many of the triphenylmethane dyes are unstable in alkaline solutions and fade rapidly. According to Heller (5), this is due to the enolization of the dye salt to the corresponding carbinol. Henriquez (6) suggested that the color change of the triphenylmethane dyes is due to the equilibrium between the aromatic and quinoid rings in the compound. He showed that the addition of an acid or a base should cause a shift in the equilibrium and that the shift should be directly proportional to the hydrogen-ion concentration of the solution. Hence it is not surprising that Patent blue V can be used as an indicator for the colorimetric determination of pH.



The triphenylmethane dyes have also been tested for use as indicators in oxidation-reduction reactions (1, 7). Like many of these indicators, Patent blue V changes from yellow to an orange-red color when it is oxidized with permanganate or ceric sulfate. Also like other dyes of the triphenylmethane series, Patent blue V is insensitive to dichromate and responds only to the stronger oxidizing agents.

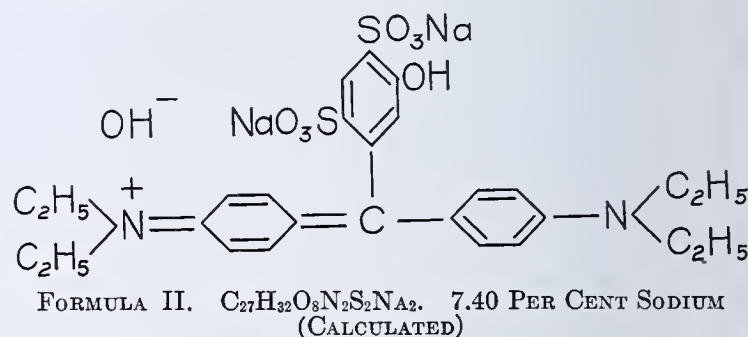
Knop (7) has investigated Patent blue A. This dye differs from Patent blue V in that it contains one  $CH_2C_6H_5$  group on each of the two nitrogen atoms in place of a  $C_2H_5$  group. Moreover, Knop's dye was the monocalcium salt. Its color transitions are similar to those of Patent blue V.

## Sources of Materials

Dyes from four different sources were used in these experiments. Sample A was obtained from E. I. du Pont de Nemours & Company, samples B and C from the General Dyestuffs Corporation, and sample D from Dr. K. Hollborn & Söhne (Leipzig). Sample E was made from sample A by extracting it with alcohol and recrystallizing twice from alcohol. Although sample A was used in the greater part of the authors' work, the others gave equally good results.

All the dye samples were tested qualitatively and no magnesium or calcium was found. However, all showed a positive test for sodium, and when sample A was analyzed quantitatively by precipitating the sodium as sodium uranyl zinc acetate, it was found to contain 14.3 per cent of sodium. Based upon Formula I,  $C_{27}H_{31}O_7N_2S_2Na$ , the compound should contain only 3.95 per cent of sodium. Sample E, the purified dye, was then analyzed

by the micromethod of Pregl (8) in which the organic matter is burned off and the sodium weighed as sodium sulfate. Duplicate analyses showed a sodium content of 7.40 and 7.63 per cent, respectively, the average being 7.52 per cent. The sample was further purified by recrystallizing twice more from alcohol and was then analyzed as before. The sodium content was found to be 7.62 per cent. As a further check on the sodium content of Patent blue V, sample D was recrystallized four times from alcohol and then analyzed. This compound contained 7.59 per cent of sodium.



These results show that the dye contains two atoms of sodium and indicate that its structure should be represented as in Formula II, rather than as in Formula I with only one atom of sodium.

Commercial Patent blue V is a dark blue or purple powder. It is highly soluble in water and alcohol, forming deep blue solutions. A 0.1 per cent aqueous solution was used in this investigation. If the volume of the solution being tested is 200 ml. or greater, a stronger solution—e. g., 0.5 per cent—of the dye may be used.

## Patent Blue V as a pH Indicator

To test the precision with which Patent blue V could be used as an indicator of pH, buffer solutions of various pH values were placed in the depressions of a spot plate and to each was added one drop of 0.1 per cent Patent blue V solution. The solutions thus formed were yellow at a pH of 0.8 and below, yellowish green to green at pH 1.2 to 2.0, took on a bluish tinge above 2.0, and finally became a pure blue at pH 3.0. The change in color is pronounced and the pH of a solution within the range of pH 0.8 to 3.0 can be determined to 0.1 pH unit by comparison with standards made up at intervals of 0.2 pH. The same dye sample must be used for both standards and unknowns, because solutions of the dye from different sources often exhibit slightly different colors at a given pH.

Buffer solutions of hydrochloric acid and sodium acetate were made from pH 0.75 through pH 3.2 according to the method of Britton (3). Check determinations were easily made upon these solutions throughout the range of pH 0.8 to 3.0. Buffers of these values were also obtained from the LaMotte Chemical Products Company and their pH values checked against the hydrochloric acid-sodium acetate solutions using Patent blue V. Color matching was made both by the spot plate method and with a roulette comparator (11) which required the use of 100 ml. of solution (in tubes 160 mm. to the mark). Check results were obtained by the two methods.

The colors formed by the indicator at the various pH values are very stable. Solutions throughout the effective range (pH 0.8 to 3.0) of the indicator were made up, using both the commercial product and the purified compound, and



allowed to stand in the diffused light of the laboratory. They were then compared at one-day intervals with freshly prepared standards using the roulette comparator. No difference in color could be detected between the aged and the fresh solutions for periods up to 5 days. At the end of 6 days a very slight fading could be detected, but no difficulty was encountered in making the match.

### Patent Blue V as an Oxidation-Reduction Indicator

Brennecke (2) noted that the transition potentials of all the triphenylmethane dyes tested for use as oxidation-reduction indicators by Knop (7), as well as those of diphenylamine, diphenylbenzidine, and many other indicators used in the oximetric titration of iron, correspond closely to the potential at the equivalence point in the ferrous-ferric system—namely, 0.77 volt. This is also true in the case of Patent blue V.

The oxidation potential of the compound was determined potentiometrically by the method of Knop (7) using a normal calomel electrode. The potentials (compared to the standard hydrogen electrode) of the various samples were found to be as follows:

	$E_0$ , Volt
Sample A	+0.75
Sample B	0.72
Sample C	0.72
Sample D	0.68
Sample E	0.78

The oxidation potential of the purified dye, sample E, corresponds almost exactly to that of the ferrous-ferric system.

Patent blue V cannot be used as a redox indicator in the titration of iron in solutions containing hydrochloric acid, on account of the dark brownish yellow color of the solution which obscures the orange color of the indicator. The yellow color is said to be due to the presence of complex anions such as  $\text{FeCl}_4^-$ . In the Zimmermann-Reinhardt method, the yellow color is removed by the addition of phosphoric acid which forms slightly ionized, colorless ferriphosphate anions. In titrations with ceric sulfate, however, a phosphate "preventive solution" cannot be used because ceric phosphate is insoluble and precipitates out of the solution before the oxidant reacts with the ferrous ion.

Szebélledy (9) showed that ammonium fluoride can be used in place of phosphoric acid to bind the ferric ions into complexes and thus remove them from solution. But ceric fluoride is insoluble and precipitates out immediately when ceric sulfate is added to a solution containing ferrous ions and fluoride ions.

Certain organic acids with which the ferric ion forms complexes were investigated in the hope of finding a solution which would reduce the concentration of the ferric ion sufficiently to allow the use of Patent blue V in titrations with ceric sulfate in the presence of hydrochloric acid. Tartaric, citric, and succinic acids were tried, but in no case was a satisfactory "preventive solution" found.

If it is necessary to reduce the iron before titration, a reduction method not requiring hydrochloric acid must be used. The Jones zinc reductor and the Walden silver reductor (10) were used in the analyses reported in Table II.

The solutions titrated should be about 1 *N* with respect to sulfuric acid and enough indicator added to impart a distinct color to the solution. Usually from 3 to 5 drops of a 0.1 per cent solution are sufficient.

As a preliminary examination of the utility of Patent blue V as an indicator in oxidation-reduction titrations, aliquot samples of a standard ferrous ammonium sulfate solution were titrated with potassium permanganate; with ceric sulfate, using *o*-phenanthroline ferrous complex as indicator; and

TABLE I. TITRATION OF FERROUS IRON

Oxidant	Indicator	Oxidizing Solution Ml.	Fe Present Mg.	Fe Found Mg.	Difference Mg.
$\text{KMnO}_4$	....	14.50	96.8	96.5	-0.3
		14.50		96.5	-0.3
		14.51		96.6	-0.2
$\text{Ce}(\text{SO}_4)_2$	<i>o</i> -Phenanthroline	15.52	96.8	97.2	+0.4
		15.50		97.1	+0.3
		15.50		97.1	+0.3
$\text{Ce}(\text{SO}_4)_2$	Patent blue V	15.49	96.8	97.0	+0.2
		15.48		96.9	+0.1
		15.48		96.9	+0.1

TABLE II. DETERMINATION OF IRON

Sample	N. B. S. No.	N. B. S. Average	Found %	Difference %
Argillaceous limestone	1	1.63% $\text{Fe}_2\text{O}_3$	1.58	-0.05
Bauxite	1		1.62	-0.01
	39	5.66% $\text{Fe}_2\text{O}_3$	5.69 <sup>a</sup>	+0.03
	39		5.70 <sup>a</sup>	+0.04
Sibley iron ore	27B	68.23% Fe <sup>b</sup>	68.33 <sup>c</sup>	+0.10
	27B		68.30 <sup>c</sup>	+0.07
Sheet brass	37B	0.21% Fe	0.18	-0.03
	37B		0.19	-0.02

<sup>a</sup> Corrected for V.

<sup>b</sup> Value recommended by National Bureau of Standards. Average value for permanganate method reported by Bureau is 68.34% Fe.

<sup>c</sup> Corrected for V and Ti.

with ceric sulfate with Patent blue V as indicator. The results are given in Table I.

The indicator is reversible. In many titrations an excess of ceric sulfate solution was added to the ferrous solution and then back-titrated to the end point. Although the color of the oxidized form fades if allowed to stand for a short time, no error is introduced if the back-titration is made within 1 or 2 minutes after the excess oxidizing agent has been added.

Several standard samples from the National Bureau of Standards were analyzed for iron, using ceric sulfate with Patent blue V as indicator. Standard methods of analysis were used for each sample. The results are recorded in Table II.

### Summary

An aqueous solution of Patent blue V may be used as an indicator for the colorimetric determination of pH over the interval 0.8 to 3.0. The colors range from yellow through green to blue and are stable for periods up to 5 days, after which a very slight fading may be detected.

Patent blue V can also be used as an oxidation-reduction indicator in certain volumetric methods. Although it cannot be used with dichromate or in the presence of hydrochloric acid, it can be used with permanganate or ceric sulfate if all hydrochloric acid is removed.

The oxidation-reduction potential of the indicator has been measured.

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# Determination of Small Amounts of Copper in Spray Residues

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**D**URING the past few years it has been necessary for the author to make a large number of copper determinations on various surfaces sprayed with copper fungicides. The surfaces upon which the copper was deposited included the leaves and fruits of apples, cherries, and tomatoes, and certain synthetic surfaces, particularly Pyralin, which is at present being used in this laboratory for most of the studies on the deposition and retention of sprays.

A number of methods have been investigated, and two have been selected as the most satisfactory under the present conditions. Since an increasing number of workers in the fields of insecticides and fungicides are turning their attention to the copper compounds, and since few rapid methods for the determination of the small amounts of copper present upon plant surfaces have been described in the literature, the following two methods are presented briefly. These are modifications of well-known analytical procedures and have been used with complete success in this laboratory for some time.

## Method A

When copper is present in the sample in amounts greater than 2 mg., the most accurate and convenient method of determination is by direct weighing after electrodeposition on platinum electrodes. The determination of small quantities (under 50 mg.) is considerably more difficult, however, than the ordinary electrodeposition as followed in the case of copper ores or alloys. The procedure found satisfactory for leaf samples which have received one or more applications of copper sprays is as follows:

A sample of from 2 to 20 grams of the dried material is ashed at a temperature not exceeding 450° C. The ash is dissolved in nitric acid (1 to 1) and transferred to a 150-ml. beaker. To this solution are added 10 ml. of a saturated solution of ammonium nitrate and 1 gram of urea, and the volume is made up to about 100 ml. The electrolysis is then carried out in the usual manner, using a platinum gauze cathode and a rotating platinum loop anode. The current between the electrodes must be much lower than is usually recommended in the methods for the electrolytic deposition of copper described in the literature, and should not exceed 0.15 ampere. Currents in excess of this amount will cause the deposition of copper oxide. The time required for complete deposition is a function of the quantity present, but for the amounts normally present on leaf samples 15 minutes is usually sufficient.

Typical results on different types of leaf material are shown in Table I.

## Method B

When the total quantity of copper in the sample is less than 2 mg., it is usually not possible to weigh the metal directly with sufficient accuracy. Samples of fruits and small areas of synthetic surfaces sprayed in the laboratory usually bear less than 1 mg., and hence require a method of analysis sensitive to smaller amounts.

After thorough trials of several methods, including the chromotropic reagent method of Ansbacher, Remington, and Culp (1), the xanthate method (2), and the thiocyanate method of Elvehjem and Lindow (4), the method of Callan and Henderson (3) as modified by Cockburn and Herd (3) was selected as most adaptable to the present use.

The method as finally adopted in this laboratory is as follows:

The solution containing the copper is freed from organic matter, if the latter is present, by digestion with sulfuric and nitric acids. For routine analysis of fruits, it has been customary to wash the surfaces thoroughly in hot 10 per cent nitric acid solution, making the washings to volume and digesting an aliquot portion. The laboratory sprayed plates are washed in 50 per cent nitric acid and the wash solution is concentrated, made to volume, and used without digestion.

The solution, free from organic matter, is neutralized with concentrated ammonium hydroxide, and about 10 ml. are added in excess. This mixture is then boiled for a few minutes, allowed to stand for 30 minutes, filtered through a fast filter paper, and washed. The entire filtrate, or an aliquot of it, is transferred to a Nessler tube, 25 ml. of concentrated ammonium hydroxide are added, and it is made to a volume of 100 ml. The tube is then placed in a photoelectric colorimeter of the type described by Frear and Haley (5) or Samuel and Shockey (6), the light intensity is adjusted to the maximum, 1 ml. of a 1 per cent solution of sodium diethyl dithiocarbamate is added, the solution is stirred, and a second reading is taken. By calibrating the instrument with known amounts of copper, the reading in microamperes may be converted directly into milligrams of copper. A typical calibration curve is shown in Figure 1.

## Accuracy of Method B

For the greatest accuracy, a sample should be selected which contains between 0.05 and 0.15 mg. of copper. Numerous recovery tests have been run with apple wash solutions containing no copper, to which have been added known amounts of copper as copper sulfate. A typical set of re-

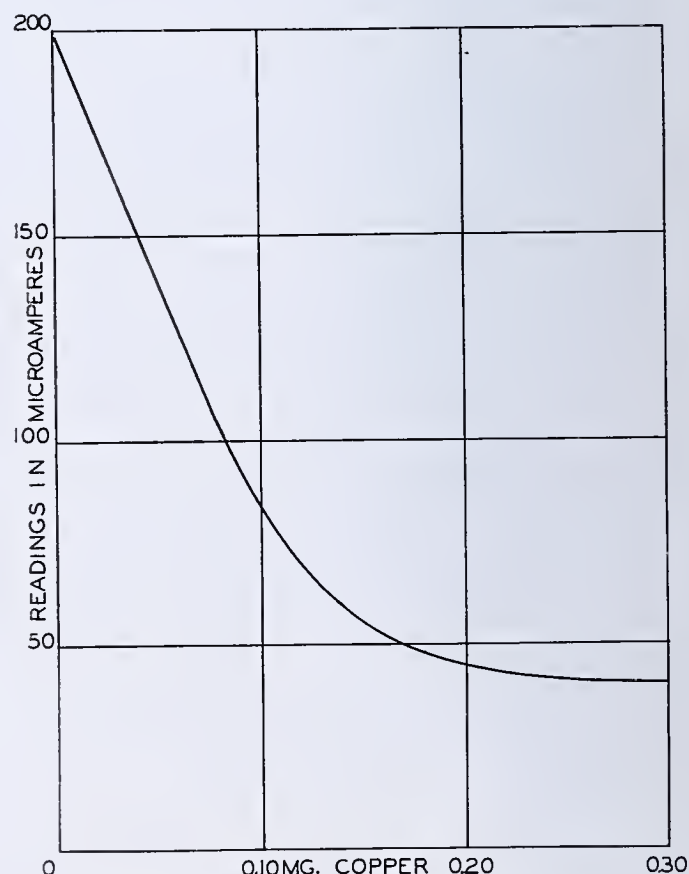


FIGURE 1. TYPICAL CALIBRATION CURVE



TABLE I. COPPER PRESENT IN APPLE AND CHERRY LEAVES AS DETERMINED BY ELECTROLYTIC METHOD			
Type of Leaf	Treatment	Copper Present	
		A	B
		Mg./sq. m.	
Apple	1 application of $\text{Cu}_3(\text{PO}_4)_2$	27.92	27.57
	1 application of Cupro-K	23.08	23.43
	2 applications of copper arsenate	65.31	64.48
Cherry	1 application of $\text{Cu}_3(\text{PO}_4)_2$	101.55	99.94
	2 applications of basic copper sulfate	26.82	25.21

TABLE II. RECOVERY OF ADDED COPPER SULFATE TO APPLE WASH SOLUTIONS		
Copper Added	Copper Recovered	
	Mg.	%
0.050	0.050	100
0.075	0.076	101
0.100	0.098	98
0.150	0.142	95

sults is shown in Table II. Each figure is the average of duplicate determinations. Replicate determinations usually agree within 2 microamperes (about 0.003 mg.).

If a photoelectric colorimeter is not available, the unknown solutions may be compared with standards in a colorimeter. In this case the color should be developed in both standards and unknowns at the same time, since the ability of the colored solution to transmit light decreases slightly on standing.

When using solutions in which no organic matter is present, such as the washings from the plates sprayed in the laboratory, the procedure may be simplified for the sake of rapidity by the elimination of the filtration, if the standardization is carried out under the same conditions.

Summary

Two methods are presented for the rapid determination of copper on surfaces sprayed with insecticide or fungicide mixtures containing this element. The first method, for quantities greater than 2 mg., is a modification of the usual procedure of weighing the metal directly after electrodeposition. The second method, for smaller quantities of copper, is based on the photoelectric measurement of the color produced by sodium diethyl dithiocarbamate.

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# Determining Riboflavin

## A Fluorometric and Biological Method

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THE establishment of riboflavin as a dietary essential has been the incentive for numerous investigations involving its biological and physico-chemical properties. Its fluorescence in ultraviolet light has suggested the possibility of utilizing this characteristic as a basis for its quantitative determination; under proper conditions as little as one part in 100,000,000 may be detected by this means. A preliminary outline of a quantitative method applicable to solutions of lactoflavin (riboflavin derived from milk) was published in 1936 (3). Since that time the method has been further perfected and applied to various materials, and also used to determine quantitatively small amounts of riboflavin required for certain precision studies involving the water-soluble vitamins (1, 4).

In order that the usefulness of any physical or chemical method for determining known vitamin entities may be fully appraised, it is necessary to correlate the results obtained with the biological response from experimental animals. The results from the fluorometric method presented in this paper have been correlated with a biological method based upon the principles of simplification and standardization previously proposed (1, 4).

Application of the fluorometric principle for the quantitative determination of riboflavin must be predicated upon the examination of appropriate solutions in which extraneous matter does not significantly interfere with the degree of

fluorescence or its observation. Potentially, each riboflavin bearing material presents a different problem in respect to the treatments required to extract the active material, and to obtain a solution suitable for examination. Obviously solutions of pure material present no such problems; likewise, many impure riboflavin concentrates, especially those obtained from whey or whey derivatives following a preliminary adsorption, frequently require no preliminary treatment other than proper dilution. Adsorbates and miscellaneous products require complete elution or extraction if reliable quantitative results are to be referred to the original carrier. The general procedure followed in the present study involves the use of an 80 per cent acetone-water mixture. Lactoflavin or natural riboflavin as derived from milk was used for the development and study of the methods hereinafter presented.

### Extraction and Preparation of Riboflavin Solutions for Fluorometric Examination

PURE OR COMPARATIVELY PURE SOLUTIONS OF RIBOFLAVIN. Such solutions of unknown concentration are diluted to match the fluorescent color of standard riboflavin solutions of known concentration.

ELUTION OF RIBOFLAVIN FROM CLAY ADSORBATES AND SIMILAR RESIDUES. A 2-gram sample is shaken with 400 ml. of an 80 per cent acetone-water (by volume) mixture in the dark at room temperature for 30 to 45 minutes, the eluate is filtered off, and the residue is washed with 10 to 15 ml. of the acetone mixture.



TABLE I. GROWTH RATE OF WHITE RATS

[From varying amounts of lactoflavin (natural riboflavin) predetermined by fluorometric method]

Period Weeks	Negative Controls (No Riboflavin)		2 $\gamma$ per Day		5 $\gamma$ per Day		10 $\gamma$ per Day		15 $\gamma$ per Day	
	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams	Cumulative Grams	Weekly av. Grams
1	2.53 $\pm$ 0.26	2.53	2.66 $\pm$ 0.37	2.66	8.20 $\pm$ 0.71	8.20	11.97 $\pm$ 0.62	11.97	14.98 $\pm$ 0.31	14.98
2	4.60 $\pm$ 0.69	2.30	4.72 $\pm$ 0.98	2.36	15.00 $\pm$ 0.95	7.50	21.90 $\pm$ 0.94	10.95	27.42 $\pm$ 0.55	13.71
3	7.61 $\pm$ 0.87	2.54	6.96 $\pm$ 1.22	2.32	20.55 $\pm$ 1.63	6.85	31.26 $\pm$ 1.64	10.42	37.69 $\pm$ 0.65	12.56
4	8.92 $\pm$ 0.89	2.23	7.84 $\pm$ 1.60	1.96	26.80 $\pm$ 2.27	6.70	39.59 $\pm$ 1.86	9.89	48.54 $\pm$ 0.95	12.13
5	10.09 $\pm$ 0.90	2.02	9.20 $\pm$ 2.00	1.84	31.75 $\pm$ 2.21	6.35	48.66 $\pm$ 2.26	9.73	59.95 $\pm$ 1.40	11.99
6	10.62 $\pm$ 0.91	1.77	10.92 $\pm$ 2.20	1.82	36.60 $\pm$ 2.41	6.10	55.88 $\pm$ 2.22	9.31	73.19 $\pm$ 1.80	12.19
7	11.22 $\pm$ 1.13	1.60	12.74 $\pm$ 2.67	1.82	39.20 $\pm$ 2.09	5.60	63.78 $\pm$ 2.32	9.11	.....	...
8	12.50 $\pm$ 1.19	1.56	13.76 $\pm$ 2.83	1.72	43.20 $\pm$ 2.14	5.40	71.00 $\pm$ 2.35	8.82	.....	...

A repetition of such elutions and washings is carried out until the final eluate shows no or at least only a slight yellow fluorescence when examined in "black light" as hereinafter described.

Following the last acetone treatment, the residue is transferred to a beaker, 25 to 30 ml. of water are added, and the suspension is boiled for 3 to 5 minutes; the suspension is then cooled and 112 ml. of pure acetone are added. This mixture is then transferred to the original elution flask, agitated for 15 to 20 minutes, and filtered, and the residue is washed with 80 per cent acetone. All eluates and washings are combined and made up to a convenient volume for preparing a series of graduated dilutions.

**PREPARATION OF SOLUTIONS FROM FLUID OR SEMIFLUID LACTOFLAVIN CONCENTRATES.** Riboflavin concentrates in fluid, semifluid, or paste form should be thoroughly mixed to assure a uniform sample. A 2-ml. or 2-gram sample is diluted 1 to 1000 with warm water or a 50 to 80 per cent acetone-water mixture. If no appreciable sediment or suspended matter is apparent, further dilutions may be made for final examination. If, however, the initial dilution shows any significant amount of sediment, flocculated, or suspended material, the original sample should be subjected to the 80 per cent acetone treatment as applied to the adsorbates.

**EXTRACTION OF LACTOFLAVIN FROM DRY WHEY AND SIMILAR WHEY PRODUCTS OR DERIVATIVES.** A 10-gram sample is eluted with 80 to 85-ml. quantities of 80 per cent acetone acidified to 0.25 *N* with sulfuric acid. This mixture is refluxed for 20 to 30 minutes, the extract is decanted or filtered, and the residue is subjected to a second or third similar treatment. Following the final extraction and filtration, the residue is washed with neutral 80 per cent acetone. The filtrates and washings are combined and made neutral to litmus with sodium hydroxide, and an aliquot sample is further diluted for final examination.

**EXTRACTION OF RIBOFLAVIN FROM MISCELLANEOUS PRODUCTS.** Various products have been subjected to the 80 per cent acetone extraction as applied to dry whey, but in all instances the refluxing periods were extended to 2 to 4 hours.

Dry yeast is heated in a drying oven at 100° C. for 5 days; the acetone in the combined extracts and washings is evaporated, and the remaining aqueous solution is neutralized and filtered prior to dilution for final examination.

Alfalfa meal, wheat bran, liver meal, and ground raw peanuts are dried to constant weight at 100° C.; neutral 80 per cent acetone is employed. The acetone from the combined extracts is evaporated and the remaining aqueous solution is washed from 3 to 10 times with petroleum ether for the removal of interfering fluorescent material, prior to diluting for final examination.

Corn meal and soybean meal are extracted in the same way as dry yeast, with the exception that the final dilutions of the soybean meal extract are made with neutral 80 per cent acetone instead of water.

### Fluorometric Examination of Riboflavin Solutions in Black Light

**PREPARATION OF STANDARD RIBOFLAVIN SOLUTIONS.** Standard solutions of riboflavin are prepared from pure crystalline material by dissolving approximately 10-mg. quantities, weighed on microbalances to within  $\pm 20$  micrograms, in 20 per cent alcohol. Such a stock solution containing 100 micrograms per ml. is used for preparing substandards with concentrations varying from 0.5 to 0.01 microgram per ml. The following concentrations are included in the series: 0.5, 0.3, 0.25, 0.2, 0.18, 0.16, 0.14, 0.12, 0.10, and thence to 0.01 microgram per ml. by 0.01-microgram intervals. The series of substandards is maintained in appropriate nonfluorescing vials of 8- to 10-ml. capacity, closed with rubber stoppers carefully cleaned by boiling 3 times with 95 per cent alcohol and finally rinsed with distilled water. If desired,

the solutions may be made up with distilled water containing 5 ml. of 40 per cent formalin per liter in lieu of 20 per cent alcohol.

**EXAMINATION IN "BLACK LIGHT."** A graduated series of dilutions of the unknown solution neutral to litmus is matched for intensity of the fluorescent color against the standard tubes of known riboflavin content. A Fluoray lamp is used as the source of "black light" (3). The observations are made in a totally darkened room or compartment against a nonreflecting and nonfluorescing black background.

The beam of ultraviolet radiation is projected directly on the tubes without intervening screen other than the standard heat-resisting red-purple filter No. 587 (manufactured by the Corning Glass Works, Corning, N. Y.), provided with the lamp and an integral part thereof. In examining certain riboflavin-bearing solutions, observations of the fluorescence may be made through filter screen No. 351 (Corning Glass Works) to eliminate the interference of blue fluorescing substances. This screen removes the blue-green radiations down to 4920 Å. It is not necessary to use this screen when examining pure riboflavin solutions or dilute solutions of riboflavin concentrates obtained as the eluate from many riboflavin adsorbates, particularly those derived from whey concentrates; likewise, its use is not recommended when suspended or colloidal material produces a gray or opalescent color in the ultraviolet rays.

At least three dilutions of the unknown sample should be made to match the intensity of the yellow fluorescence of the standard solution tubes within the range of 0.02 to 0.1 microgram per ml. (The readings at the three concentrations should check in accordance with the known dilution of the unknown. For example, if dilution *A* of the unknown matches the intensity of the fluorescent color of the standard tube containing 0.08 microgram per ml., dilution *B* of the unknown prepared by diluting *A* with an equal volume of distilled water should check the standard tube containing 0.04 microgram per ml., etc.) For greater precision a fourth dilution of the unknown may be made, using the three concentrations within the range mentioned and the fourth concentration to match one of the standard dilutions within the 0.1- to 0.2-microgram range. The average calculated riboflavin content as determined by the multiple readings is the reportable value.

**PRECAUTIONS.** All standard solutions should be stored in total darkness and all unnecessary exposure to the ultraviolet radiation avoided. At least one reserve set of standard solution tubes should always be kept shielded from all light. At frequent intervals the standard dilutions in current use should be compared with the reserve set. If there is distinguishable fading of the fluorescent color, particularly at the lower concentrations, or if there is a bluish haze in the standards employed for assay purposes, such manifestations are evidence of gradual destruction of the riboflavin. The tubes should be immediately replaced by new standards in which no such deterioration has taken place.

### Biological Method for Determining Riboflavin

The biological method for determining riboflavin, as used for determining the correlation of the animal response with the riboflavin content of various materials as determined by the fluorometric method, follows.

White rats 22 to 25 days old weighing 40 to 50 grams are placed in individual metal cages with screened bottoms and supplied a basal ration of the following composition: vitamin-free casein (Labco, distributed by the Borden Co., Labco Products Department, 350 Madison Ave., New York, N. Y.), 20 parts; sucrose, 69 parts; hydrogenated vegetable oil (Crisco), 3 parts; salt mixture No. 40 (2), 4 parts; powdered agar-agar, 2 parts;



TABLE II. GROWTH RATE OF WHITE RATS

[From varying amounts of lactoflavin (natural riboflavin) predetermined by fluorometric method and carried by fuller's earth adsorbates]

Period Weeks	Sample B1454, 19.7 Mg. = 5γ per Day		Sample B1454, 59 Mg. = 15γ per Day		Sample B1458, 51.5 Mg. = 15γ per Day		Sample B1459, 16.6 Mg. = 5γ per Day	
	Cu- mula- tive Grams	Weekly av. Grams	Cu- mula- tive Grams	Weekly av. Grams	Cu- mula- tive Grams	Weekly av. Grams	Cu- mula- tive Grams	Weekly av. Grams
1	6.97	6.97	12.97	12.97	14.47	14.47	7.97	7.97
2	13.46	6.73	28.46	14.23	24.96	12.48	15.71	7.85
3	17.14	7.05	33.39	11.13	34.39	11.46	22.14	7.38
4	24.58	6.14	44.58	11.14	43.58	10.89	26.83	6.71
5	27.66	5.53	52.16	10.44	57.66	11.53	32.16	6.44
6	32.66	5.44	65.13	10.86	70.63	11.77	35.63	5.94

resumed and soon becomes established at a rate commensurate with the amount of riboflavin supplied.

Negative control groups receiving the basal ration and the primary riboflavin-free supplement should be maintained throughout the assay period. Growth response due to riboflavin is computed as the difference between that shown by the negative controls and that induced by the sample through a period of not less than 4 weeks and not exceeding 8 weeks. This method for determining growth response due to variable amounts of lactoflavin was employed in determining the values shown in Figures 1 and 2 and Tables I, II, and III.

Correlation of Results from Fluorometric and Biological Methods

The following data correlating the riboflavin determinations as made by the fluorometric method with the results obtained from the biological method involve numerous comparisons extending over a period of about 2 years. An equal number of male and female animals are represented in each comparison. All quantities of riboflavin indicated as being fed in known amounts were computed from the results obtained by the fluorometric method. Tables I and II and Figure 1 show the results obtained from riboflavin provided in pure form and as carried by fuller's earth adsorbates.

The data from the variable amounts of pure riboflavin show a substantially uniform and constant rate of growth for a period of 6 to 8 weeks commensurate with the amount provided. However, the different rates of growth are not maintained at exactly the same mathematical ratio at which the riboflavin was fed. The ratio between the average rate of growth per week from the 2- and 5-microgram levels is 1 to 3.08 instead of the theoretical 1 to 2.5; from the 2- and 10-microgram feedings it is 1 to 4.89 or very close to the theoretical 1 to 5 ratio; from the 2- and 15-microgram levels it is 1 to 6.04 instead of 1 to 7.5; from the 5 to 15 levels the ratio is 1 to 1.86; and from the 10 to 15 levels it is 1 to 1.85.

From these comparisons it might be concluded that the most reliable range of growth rate lies between 6 and 10 grams per week for not less than 4 weeks and not more than 8 weeks. Such a rate of growth conforms fairly well to the calculated gain per week attributable to each microgram of riboflavin per day, as it is to be noted that the average rate of growth per week from the 2 micrograms per day feeding is 2.06 grams, or the equivalent of 1.03 grams per microgram. On the basis of this computation the theoretical rate of growth at the 5-microgram level should be 5.15 grams per week, whereas the data show an average of 6.58 grams; the theoretical rate at the 10 micrograms per day level should be 10.30 grams per week; the actual average is 10.16 grams. These results substantiate the general conception that 2 to 3 micrograms of lactoflavin per day are necessary to induce a 3-gram gain per week, this amount being equivalent to 1 Bourquin-Sherman unit of vitamin G or B<sub>2</sub>.

The growth response obtained from experimentally and commercially produced fuller's earth adsorbates (Table II) fed at predetermined levels calculated to carry 5 and 15 micrograms of riboflavin as determined by the fluorometric method, is substantially the same as that obtained from the same amount of riboflavin fed in pure solution, the correlation being from 92 to 98.6 per cent. While this correlation in biological response based in turn upon the values obtained by the fluorometric method is considered remarkably close, and serves to show that the riboflavin carried by such adsorbates is fully available to the animal, or substantially so, such deductions are not applicable to all riboflavin adsorbates.

Various carbons are known to be highly efficient adsorbants for riboflavin, but removal of the riboflavin from such

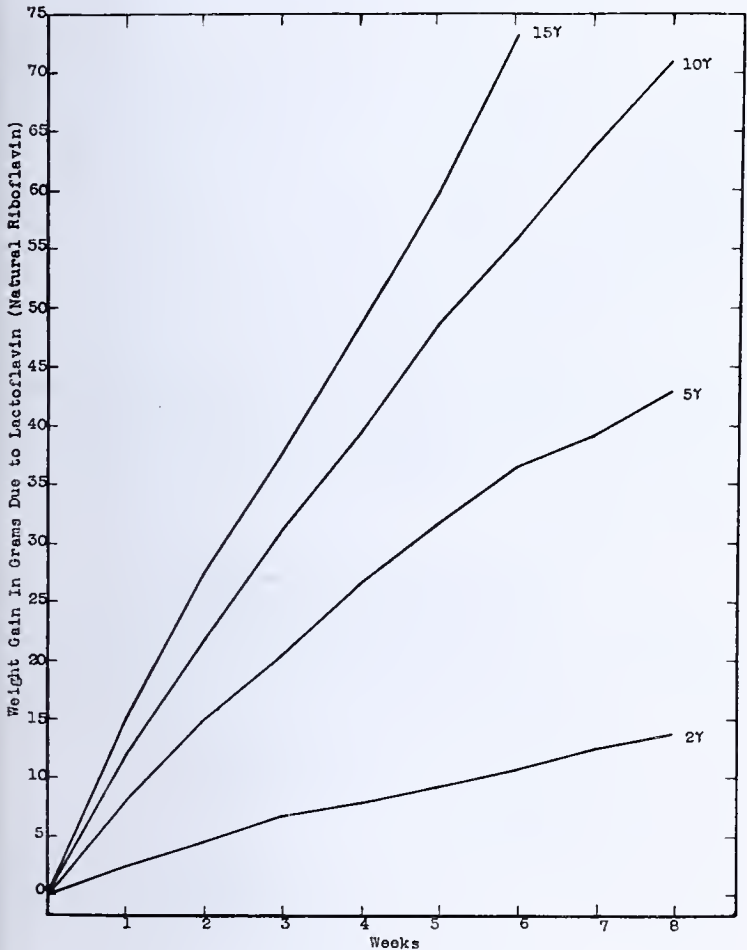


FIGURE 1. GROWTH RATE OF WHITE RATS

Varying amounts of lactoflavin (natural riboflavin) per day as predetermined by the fluorometric method

and cod liver oil, 2 parts. The animals are maintained on this unsupplemented diet for 1 to 2 weeks, during which constant or declining weight is established. Only an insignificant gain in weight takes place during this period. At this point the following supplements are provided per rat per day: 12.5 micrograms of pure vitamin B<sub>1</sub> (Merck or equivalent) and 100 mg. of autoclaved rice polish concentrate (Labco). The rice polish concentrate available in desiccated form is dissolved in water at a 7.5 per cent concentration, the pH adjusted to 8.5, and the alkaline solution autoclaved 5 hours at 120° C. These supplements are fed together in aqueous solution, the requisite amount being carried in 2.5 to 3.5 ml. supplied in small glass caster cups.

Growth is stimulated for a short period following introduction of the riboflavin-free water-soluble factors provided by this supplement. Constant weight or a rate of gain in weight not exceeding about 1 to 2 grams per week is again established after a period of about 2 to 3 weeks. At this point the animals are considered in proper condition for receiving the unknown material for the riboflavin assay. Graduated amounts of the assay sample are supplied to different groups of animals each day in addition to the primary supplements. Growth is immediately



adsorbates is not easily accomplished by ordinary means. In order to determine comparative differences in the retention properties of fuller's earth and carbon adsorbates, riboflavin solutions of known concentration were adsorbed on these materials, and the adsorbates were thoroughly washed and subjected to the 80 per cent acetone elution treatment, and likewise tested by the biological method. The fuller's earth adsorbate permitted a growth response calculated to be the equivalent of 96 per cent of that resulting from the same amount of riboflavin fed in pure solution. The carbon adsorbate eluted with 80 per cent acetone yielded only a trace of riboflavin. When subjected to the biological test in quantities known to contain from 5 to 50 micrograms (16.7 to 166.7 mg. of carbon) no growth resulted, indicating conclusively that the animal was unable to utilize the riboflavin adsorbed on these particular carbons. The results from the 166.7-mg. quantities carrying 50 micrograms of riboflavin indicated not only that the animal was unable to release the riboflavin, but also that the carbon actually adsorbed from the intestinal tract the water-soluble supplements supplied with the basal ration (Figure 2).

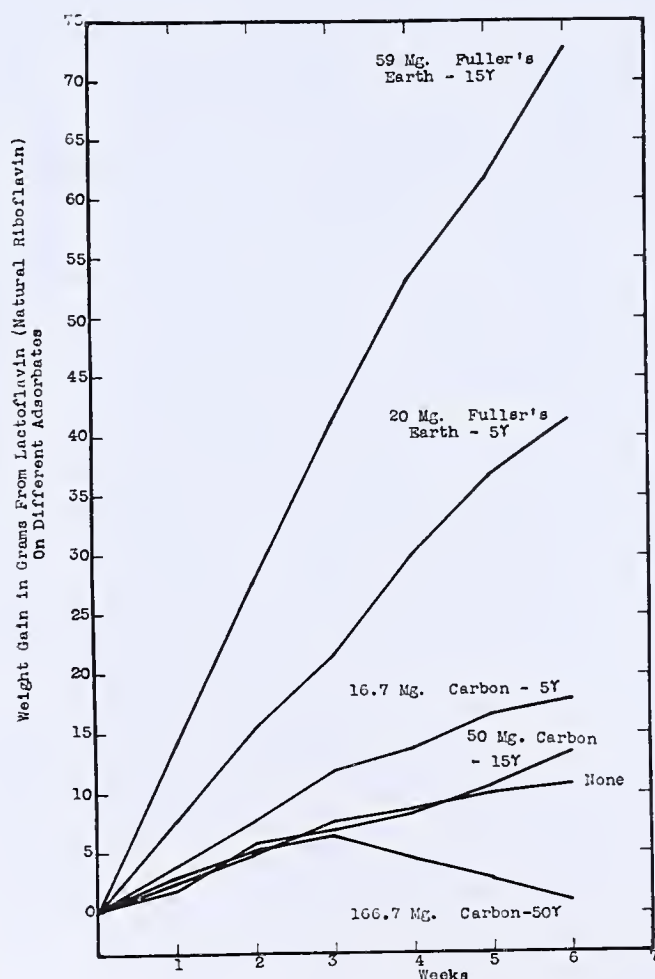


FIGURE 2. GROWTH RATE OF WHITE RATS

Varying amounts of lactoflavin (natural riboflavin) per day as carried on fuller's earth and carbon adsorbates

The correlation of the results from the fluorometric and biological method as applied to miscellaneous products was ascertained by first determining the riboflavin content fluorometrically. The milligrams of substance required to furnish given amounts of riboflavin were calculated; these calculated quantities were fed to the test animals daily to determine how the growth response compared with that obtained from solutions of known riboflavin content and of proved biological potency. By using the growth per week attributable to 1 microgram of riboflavin per rat per day as

shown by the basic data (Table I) it was possible to interpret the growth response from the test products in terms of the amount of riboflavin contained in each. A comparison of the results from the two methods is shown in Table III, from which it will be noted that while the values from yeast and peanuts are closely comparable, those from alfalfa meal and liver meal are less satisfactory; the results from the soybean meal and corn meal are at variance by more than 50 per cent.

It would appear from these results that the fluorometric and biological methods cannot be employed interchangeably for all miscellaneous products with assurance that the same interpretation of riboflavin content will result. However,

TABLE III. CORRELATION OF RIBOFLAVIN CONTENT OF MISCELLANEOUS PRODUCTS

(Determined by fluorometric and biological methods)

Product	Amount Fed per Day Mg.	Fluorometric Method $\gamma$ riboflavin per gram	Biological Method	Percentage Correlation
Alfalfa meal	227	33.2	28.4	85
Raw peanuts	1111	4.5	4.7	95
Dry yeast	87	71.2	73.0	97
Liver meal	54	85.0	68.0	80
Soybean meal	526	19.0	8.5	45
Corn meal	455	4.5	10.7	42
Corn meal	1351	4.5	10.7	42

comparable values obtained from riboflavin solutions, concentrates, adsorbates, and yeast indicate that the methods are equally reliable. Because of discrepancies in results obtained from other products, the fluorometric method can be considered primarily as a qualitative comparison method for such products.

### Summary and Conclusions

Fluorometric and biological methods for determining riboflavin have been described which give concordant results and show a 95 to 96 per cent correlation when applied to pure riboflavin solutions of unknown concentration, riboflavin concentrates obtained as eluates from fuller's earth, and fuller's earth adsorbates. Neither method is of value when applied to carbon adsorbates.

Both methods show in excess of 90 per cent correlation when applied to dry yeast and raw peanuts; from 80 to 85 per cent when applied to alfalfa meal and liver; and less than 50 per cent correlation when applied to soybean meal and corn meal.

One microgram of lactoflavin (natural riboflavin derived from milk) per rat per day causes a growth response of substantially 1 gram per week for a period of 6 to 8 weeks through a 2- to 10-microgram per day feeding range.

The fluorometric and biological methods may be used interchangeably for certain types of riboflavin solutions and adsorbates with equal reliability. The fluorometric method applied to such types of riboflavin-carrying materials gives consistent check results within 10 per cent variation from independent determinations and different operators; more experienced operators readily obtain check results within 3 to 5 per cent variation.

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# Calibration of Weights

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**A rigorous modification of Richards' method is described, including standardization in terms of a standard reference mass. Its advantages are mechanical simplicity, ease of checking for arithmetical errors, and wide applicability. A mathematical discussion of the validity of Richards' method is given.**

THE methods of weight calibration thus far described follow Kohlrausch (6, 8), Richards (10), or Benoit (2). Kohlrausch and Benoit employed a direct method, in which group weighings give rise to sets of simultaneous linear "computational equations." By solving these equations, the error in each of the weights is found. Richards, on the other hand, determined the relative magnitude of each weight in terms of the smallest, thereby obtaining an arbitrary but self-consistent series of values. Of these methods, Richards' is the simplest, both in theory and in application.

The procedure here described, based on Fales' modification (4) of Richards' method, avoids algebraic manipulations, and is applicable to any of the common sequences of weights, and to certain sets of weights which do not form a sequence, without setting up equations and without changes in the procedural details.

The work falls naturally into two parts: the weighings, and the calculations. The first part has for its object the determination of a set of self-consistent relative values for the weights, while the second part concerns itself with converting the relative values into absolute c. g. s. units, using a certificated reference mass as the standard.

## Weighings

In determining the relative values, each weight in turn is compared with a suitable group of its predecessors, as shown below, the rider being arbitrarily assigned a relative value equal to its denominational value. Commonly the 5-mg. weight is used, but as pointed out by Hurley (5) this may be a source of error. Since interpolative weighings depend on the sensitivity, which in turn depends on the assumed weight of the rider, there are two unknowns—the 5-mg. weight and the rider. The difficulty may be avoided by either of two devices. The first is to make the rider itself the basis of the relative system, thereby producing a system with only one unknown. The other way, practical but not rigorous, is to retain the two unknowns, but first to "prove the rider" as described by Fales (4, section 83). In the latter method, care is taken that the rider agrees closely with the 5-mg. weight. If the agreement is not within the probable error of a weighing, a different rider should be chosen. In general, it is urgent that the rider be very close to its denominational value in order to avoid an inconvenient correction which depends upon the location of the rider.

By means of the weighings, the relative values are all determined—that is, the 5-mg. weight is known in terms of the rider; the 10 in terms of the 5 and the rider; the 20 in terms of the 10, 5, and rider; and so on, to the largest weight of the set. In order to convert this self-consistent set of values into the standard c. g. s. values, the magnitude of the "relative unit" must be found in terms of the c. g. s. system. To this end it is necessary and sufficient to know the value of some

large weight in terms of both systems. The standard reference mass is convenient for this, its c. g. s. value being already known, and its relative value being easily found by comparison with the others. The quotient of the two values is a multiplying factor for changing relative into absolute. The large number of significant figures involved in such a computation makes it worth while to consider an indirect method for carrying out the work.

## Calculations

Let us consider some of the mathematical properties of the proportion

$$\frac{a}{r} = \frac{A}{R} \quad (1)$$

Upon applying "alternation" and "division," we have

$$\frac{a - A}{r - R} = \frac{A}{R} \quad (2)$$

Or, if we had multiplied by the arbitrary factor  $1/n$ , prior to these operations

$$\frac{a - A/n}{r - R/n} = \frac{A}{R} \quad (3)$$

Whence

$$a = \frac{A}{R} (r - R/n) + \frac{A}{n} \quad (4)$$

The proof of these derived forms may be had by multiplying out and canceling, thus arriving immediately at the original proportion, Equation 1.

Richards stated that his method depended on "the properties of small numbers in the presence of large ones," and a number of attempts have been made to explain this or to disprove it. For example, it has been discussed by Eaton (3), and further developed by Hurley (5). From a practical point of view these authors conclude Richards' method to be correct, but they fail to point out the mathematical basis of the method.

Referring to the foregoing equations, let  $A$  and  $a$  refer to the absolute c. g. s. values;  $R$  and  $r$  to the arbitrary relative values. The capitals refer to the certified standard of mass, while the lower-case letters refer to each particular weight of the set, in turn.  $A/R$  is seen to be the conversion ratio already mentioned. Values  $r$  are the observed data, the relative values. The ratio  $A/R$  is not applied directly to the values  $r$ , but to a derived quantity,  $r - R/n$ , in which  $n$  is so chosen as to make the whole quantity extremely small. The latter condition is fulfilled if  $n$  is taken as the ratio of the nominal value of the standard to each nominal weight in turn. Values  $n$  are then whole numbers or simple fractions (Table I).

With  $n$  chosen in this manner, quantities  $r - R/n$  become the corrections to the "relative aliquots," and they are of the same order as the final corrections. These values multiplied by the conversion ratio,  $A/R$ , give the corrections to the "absolute aliquots," where the term "aliquot" means the  $n$ th submultiple of the value of the standard weight in either system. This mathematical trick for simplifying the arithmetic depends on the properties of equal ratios; hence it is no approximation, but is rigorous.

Richards followed the same procedure as given here, up to the formation of the corrections to the aliquots, which he left in that form, calling them the final corrections. Using the same nomenclature as above, but letting  $w$  represent the final adjusted values and  $W$  the assumed standard value of



TABLE I. BEGINNING OF TABULAR COMPUTATION							
(Ratio $A/R = 49,998.00/49,601.75 = 1.008$ )							
1	1a	2	3	4	5	6	7
Denomi- nation, Grams	Sub- multi- ple $n$	Relative Values $r$	Relative Aliquots $R/n$	Relative Differ- ences $r - R/n$	Absolute Differ- ences $(r - R/n) \times A/R = a - A/n$	Absolute Aliquots $A/n$	Absolute C. G. S. Values $(a - A/n) + A/n = a$
100	1/2	99,211.53					
50, standard	1	49,601.75	49,601.75	****	****	49,998.00	49,998.00
50	1	49,606.02					
20	5/2	19,842.35					
10	5	9,920.95					
10	5	9,920.83					
5	10	4,960.64					
..	....	.....					
..	....	.....					
..	....	.....					
Mg.							
10	5,000	10.07					
10	5,000	10.06					
5	10,000	4.92					
5, rider	10,000	5.00					

the reference weight (Richards assumed  $W = 10.00000$  grams), we have

$$w = r \frac{W}{R} = r \frac{1}{R/W} = r \frac{1}{1 - \left(\frac{W - R}{W}\right)} \tag{5}$$

a rigorous equation, which Richards approximated as follows:

$$w = r \frac{1}{1 - \left(\frac{W - R}{W}\right)} \doteq r \left[ 1 + \left(\frac{W - R}{W}\right) \right] = r + \frac{W - R}{W/r} \tag{6}$$

$$w \doteq r + \frac{W - R}{W/r} \doteq r + \frac{W - R}{n} = \frac{W}{n} + \left(r - \frac{R}{n}\right) \tag{7}$$

The first approximation comes from discarding all terms except the first two, in the infinite binomial series. The second approximation involves the substitution of the coefficient  $n$  (equal to  $R/r = W/w$ ) for the quantity  $W/r$ . Comparison of this with Equation 4 shows the true equation to be

$$w = \frac{W}{n} + \frac{W}{R} \left(r - \frac{R}{n}\right) \tag{8}$$

Hence there is a third approximation, in that  $W/R$  is taken to be unity, which is all right in most cases, but not in all (in

Table II, see the corrections to the 100-gram, 50-gram, and 20-gram weights). Therefore Richards' system depends not only upon "the properties of small numbers in the presence of large ones" in the sense intended (7), but also upon the relative magnitude of the units in the  $w$  system and in the  $r$  system.

PROCEDURE. Following Richards, the tabular form of computation is used, all computations being done directly in the table, without recourse to scratch paper, except in the case of the division  $A/R$ . Orderliness and convenience are the great advantages of the arrangement, which makes for rapid, systematic prosecution of the work. The arrangement's simplicity makes for ease of checking, a point that is too often insufficiently emphasized. The author's experience is that workers of all types are far more prone to mistakes in the computations than in the observations. In the tabular arrangement, mistakes may be located almost at a

glance—for example, a skilled computer required slightly less than 5 minutes, actual timing, for checking all the computations of Table III.

Referring to Table I, let it be assumed that the relative values have been obtained, including that of the standard weight. They are listed in descending order, to the nearest 0.01 mg. (actual precision may be from 0.03 to 0.08 mg.), in column 2. Thus far the absolute value is known for only one weight—the standard, in this case assumed to be a 50-gram weight. This value appears in the appropriate place in column 7. The relative and absolute values of the standard weight are also placed in columns 3 and 6, respectively, under the headings of "aliquots."

When these figures have been entered, the aliquot columns are next filled in by writing the successive fractional parts or aliquots of the standard weight in each line, according to the denominations in column 1. The factor  $n$  is given in column 1a, and is the ratio of the denominational value of the standard to each denominational value in turn. In arriving at the aliquot corresponding, for example, to the 20-gram weight, the value of the standard is divided by 5/2. For the 10-gram weight, the divisor is 5, and so on down the line. All the lesser aliquots are simply obtained from those for 50, 20, and 10, by merely shifting the decimal point to the left.

It will be found in practice that the relative aliquots differ very little from the relative values of the weights to which

TABLE II. CONTINUATION OF COMPUTATION						
(Ratio $A/R = 1.008$ )						
1	2	3	4	5	6	7
Denomi- nation, Grams	Relative Values $r$	Relative Aliquots $R/n$	Rela- tive Differ- ences $r - R/n$	Ab- solute Differ- ences $(r - R/n) \times A/R$	Absolute Aliquots $A/n$	Absolute C. G. S. Values $a$
100	99,211.53	99,203.50	8.03	8.09	99,996.00	100,004.09
50, standard	49,601.75	49,601.75	****	****	49,998.00	49,998.00
50	49,606.02	49,601.75	4.27	4.30	49,998.00	50,002.30
20	19,842.35	19,840.70	1.65		19,999.20	
10	9,920.95	9,920.35	0.60		9,999.60	
10	9,920.83	9,920.35			9,999.60	
5	4,960.64	4,960.18			4,999.80	
..	.....	.....			.....	
..	.....	.....			.....	
..	.....	.....			.....	
Mg.						
10	10.07	9.92			10.00	
10	10.06	9.92			10.00	
5	4.92	4.96			5.00	
5, rider	5.00	4.96			5.00	



TABLE III. COMPLETE COMPUTATIONS FOR A 1-2-3-5 SEQUENCE								
(Ratio A/R = 100,000.20/99,567.22 = 1.004)								
1	2	3	4	5	6	7	8	9
Denomi- nation Grams	Relative Values	Relative Aliquots	Rela- tive Differ- ences	Abso- lute Differ- ences	Absolute Aliquots	Absolute Values	Rounded Values	Correc- tions in 0.1 Mg.
100, standard	99,567.22	99,567.22	****	****	100,000.20	100,000.20	Standard	Value
50	49,782.14	49,783.61	-1.47	-1.48	50,000.10	49,998.62	49,998.6	-14
30	29,870.71	29,870.16	0.55	0.55	30,000.07	30,000.62	30,000.6	6
20	19,913.49	19,913.44	0.05	0.05	20,000.04	20,000.09	20,000.1	1
10	9,957.02	9,956.72	0.30	0.30	10,000.02	10,000.32	10,000.3	3
5	4,978.52	4,978.36	0.16	0.16	5,000.01	5,000.17	5,000.2	2
3	2,987.09	2,987.02	0.07	0.07	3,000.01	3,000.08	3,000.1	1
2	1,991.34	1,991.34	0.00	0.00	2,000.00	2,000.00	2,000.0	0
1	995.72	995.67	0.05	0.05	1,000.00	1,000.05	1,000.1	1
Mg.								
500	497.86	497.84	0.02	0.02	500.00	500.02	500.0	0
300	298.68	298.70	-0.02	-0.02	300.00	299.98	300.0	0
200	198.94	199.13	-0.19	-0.19	200.00	199.81	199.8	-2
100	99.60	99.57	0.03	0.03	100.00	100.03	100.0	0
50	49.75	49.78	-0.03	-0.03	50.00	49.97	50.0	0
30	29.88	29.87	0.01	0.01	30.00	30.01	30.0	0
20	19.87	19.91	-0.04	-0.04	20.00	19.96	20.0	0
10	9.93	9.96	-0.03	-0.03	10.00	9.97	10.0	0
5	4.99	4.98	0.01	0.01	5.00	5.01	5.0	0
5, rider	5.00	4.98	0.02	0.02	5.00	5.02	5.0	0

they correspond. This fortunate circumstance is an important feature of the method, since the next operation is to subtract algebraically the aliquots from the relative values. The differences are placed in column 4. The progress of the work so far is shown in Table II, in which the aliquot columns

terms of a 100-gram Bureau of Standards certi-  
ficated weight as a primary reference standard.  
It was found convenient to conduct the standardi-  
zation in groups of five, using a 50-gram auxiliary  
weight to make up the total of 100 grams. There  
is no reason for not calibrating ten at a time  
except the possibility of confusion attendant upon  
the use of so many outwardly identical objects  
at once. The actual computation is shown in  
Table IV. One of the 10-gram weights was as-  
sumed to weigh exactly 10,000 arbitrary relative  
units, and the weights of the others were found  
by intercomparison. The computation for the  
absolute value of the 50-gram weight was carried  
through in each case, in order to compare the  
several values thereby found. This served as  
a partial check upon the group calibrations.  
This method is at least as precise as any of the  
methods now in use. If greater precision is de-  
sired, it must be sought by the use of multiple  
weighings, as, for example, in the method of  
Benoit (1, 2, 9) in which the method of least  
squares may be used for adjusting the residues.  
For the set of weights first described, thirty-one  
weighings were necessary, using Borda's substi-  
tution weighing. This may seem disadvan-  
tageous when it is considered that by suitable grouping of the  
weights the number of weighings may be reduced to twenty-  
two, but in such a case it is necessary to set up and solve a  
set of simultaneous equations, different for each sequence of  
weights.

TABLE IV. COMPARISON OF SECONDARY STANDARDS IN GROUPS OF FIVE						
(Ratio A/R = 100,000.30/99,999.26 = 1.00001)						
1	2	3	4	5	6	7
Denomination and Description Grams	Relative Values	Relative Aliquots	Relative Differ- ences	Absolute Differ- ences	Absolute Aliquots	Absolute C. G. S. Values
100, N. B. S. test	99,999.26	99,999.26	****	****	100,000.30	100,000.30
50, auxiliary	49,999.94	49,999.63	0.31	0.31	50,000.15	50,000.46
10, No. 6	10,000.00	9,999.93	0.07	0.07	10,000.03	10,000.10
10, No. 7	9,999.87	9,999.93	-0.06	-0.06	10,000.03	9,999.97
10, No. 8	9,999.62	9,999.93	-0.31	-0.31	10,000.03	9,999.72
10, No. 9	10,000.18	9,999.93	0.25	0.25	10,000.03	10,000.28
10, No. 10	9,999.99	9,999.93	0.06	0.06	10,000.03	10,000.09

have been filled in, and the first few subtractions written in  
column 4. These differences never contain more than three  
significant figures, and usually not more than two. They are  
all of the order of milligrams or less.  
When the subtractions have all been performed, the next  
step is changing the differences to absolute values, through the  
ratio A/R. These results, the "absolute differences," are to  
be written in column 5. Upon adding these algebraically to  
the absolute aliquots in column 6, the absolute values are  
obtained; these are written in column 7. The computation  
is best completed columnwise, each column being worked  
upon in turn, thereby grouping all subtraction operations, all  
divisions, all additions, etc. To illustrate the versatility of  
the method, complete computations are given in Table III for  
a set of weights of the 1-2-3-5 sequence. Columns 8 and 9  
of Table III give, respectively, the values rounded off to the  
precision limits and the list of corrections.  
The method has been in use for three years with quantita-  
tive analysis classes, with a high degree of success. It has  
been found useful not only for calibration of weights in sets,  
but also for the calibration of certain secondary standards of  
mass. These are of 10 grams each, and were calibrated in

For accuracy and simplicity, without algebraic complica-  
tion, the present method is far in the lead. Its advantages  
may be summed up as simple theory, logical arrangement,  
directness of the computation, ease of checking for errors, and  
applicability to all sequences without change. For an extended  
list of additional references, see (11).

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# Hydrogen Peroxide in the Colorimetric Determination of Iron by Thiocyanate

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IN DETERMINING iron colorimetrically by the thiocyanate process it is customary to oxidize the iron by permanganate. Van Urk (9) used permanganate followed by peroxide or persulfate. The authors have preferred to use peroxide alone, as its use avoids the introduction of the highly reactive manganese ion and of sulfates. That sulfates are undesirable is indicated by the work of Hedenström and Kunau (3), who studied the effect of salt concentration on the discharge of the red iron-thiocyanate color. Calculation from their data shows that the salt-thiocyanate ratio for effective color discharge is four times as great for chlorides as for sulfates. One would naturally assume, then, that sulfates are four times as effective as chlorides in preventing the development of the red color and so to be avoided whenever possible.

It is known (4) that powerful oxidizing agents produce yellow substances from thiocyanate, particularly at higher temperatures, although Sharma (7) says that pure ammonium thiocyanate, from which traces of iron have been removed, does not give a color with peroxide, hydrochloric acid, or chlorine. Sharma also further states, as do Patten and Smith (5), that traces of iron are present in thiocyanates. Evidently the ordinary thiocyanate reagent contains traces of iron and is customarily used with this impurity present, as noted by Winsor (10).

To ascertain the effect of hydrogen peroxide in producing colored substances in sodium thiocyanate solutions to which no iron had been added, a normal sodium thiocyanate solution was made 0.18 *M* with hydrogen peroxide and allowed to stand overnight. A yellow precipitate and a red solution were present next morning. To find out how much hydrogen peroxide can be used safely, other experiments were made in which peroxide was mixed with thiocyanate with and without hydrochloric acid. The data are collected in Table I.

TABLE I. COLOR PRODUCED IN THIOCYANATE SOLUTIONS

(Varying amounts of hydrogen peroxide and hydrochloric acid)

Tube No.	CNS, <i>N</i>	0.68 Per Cent H <sub>2</sub> O <sub>2</sub> , <i>M</i>	HCl, <i>N</i>	Remarks
		<i>ML.</i>		
1	0.4	0.25	0.001	No color
2	0.4	0.25	0.001	Slight yellow color on mixing
3	0.4	0.74	0.003	No color
4	0.4	0.74	0.003	Slight yellow color on mixing
5	0.4	0.74	0.003	Slight yellow color on mixing
6	0.3	0.2	0.0008	
7	0.3	0.4	0.0016	
8	0.3	0.6	0.0024	Very slight color in all tubes
9	0.3	0.8	0.0032	
10	0.3	0.2	0.0008	
11	0.3	0.8	0.0032	
12	0.2	0.2	0.0008	No color
13	0.2	1.0	0.004	Very slight color
14	0.2	1.0	0.004	Very slight color

It is evident that color develops with lower concentrations of peroxide and thiocyanate when the solution is acid. A solution develops no color when it is 0.2 *N* in thiocyanate, 0.01 *N* in acid, and 0.0008 *M* in peroxide. Increasing thiocyanate one and one-half times, peroxide ten times, or acid ten times, produces a very slight yellowish color, but this color is too slight to be of analytical importance and the authors frequently exceeded these amounts without noticeable

effect. The figures indicate that a solution about 0.0024 *M* with peroxide is of satisfactory strength.

Practically, to get the right amount of peroxide it is not necessary to standardize the peroxide solution. Instead, to three tubes, containing the same quantities of acid, iron, and thiocyanate, definite varying amounts of peroxide are added—say, 10, 20, and 30 drops, respectively. If the 10- and 20-drop tubes give the same color and the 30-drop tube is slightly yellowish, the limits are thereby set as 10 to 20 drops. Further, if a solution of peroxide is standardized two or three times at intervals of some days or weeks further standardization is unnecessary, as the subsequent strength of the solution can be read from the straight-line graph expressing the ratio of moles per day.

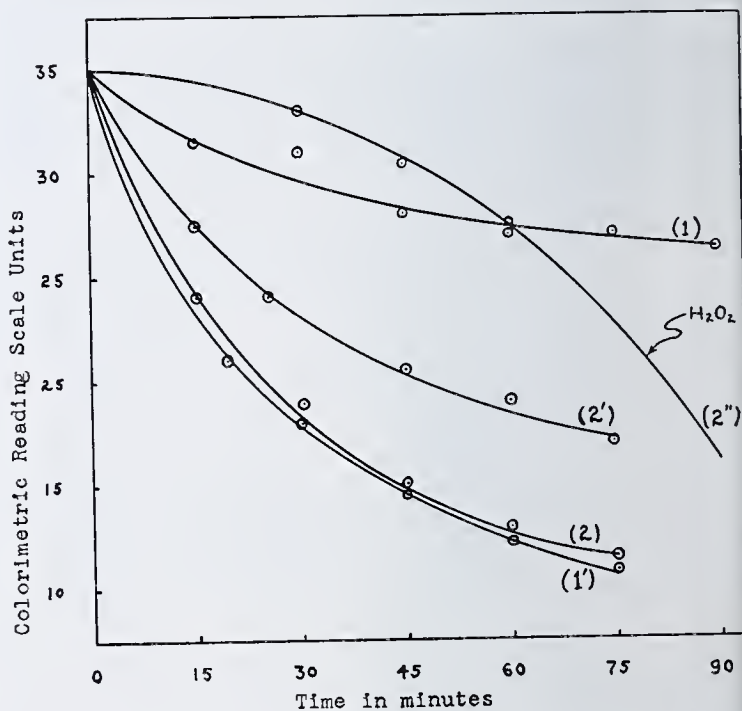


FIGURE 1. RATE OF FADING OF FERRIC THIOCYANATE

Fe, p. p. m. Fe/CNS 1/9280. HCl/CNS 0.01/0.16 *N*

1. March 6, cloudy, dark  
1', 2'. July 1, bright  
2, 2''. March 16, mostly bright

Acid alone with ordinary analytical grade of thiocyanate will produce colored substances but not, as the authors found, if kept below 0.1 *N* when the thiocyanate is as high as 0.4 *N*.

The use of permanganate for oxidizing iron necessitates a reading at the moment the permanganate fades, in order to avoid negative error. With hydrogen peroxide the iron thiocyanate color lasts for some time. To study the fading of the red color, experiments were made both with and without hydrogen peroxide, no permanganate being used. The colorimetric reading was plotted against time and zero time was set at 35 scale units. The results are shown in Figure 1.

It is evident that without peroxide (curves 1, 1', 2, 2'), the fading is rapid, while with 0.0028 *M* peroxide (curve 2'') the color is stable for at least 5 minutes. Curve 1 was made on a cloudy day in March, curve 2 on a bright day in March, and 1' and 2' on a bright day in July, all exposed to north



light. The much faster fading in bright light is in conformity with the findings of other workers (1, 2, 6, 8). In other experiments carried out in tall Nessler tubes of 50-ml. capacity the amount of hydrogen peroxide was increased and the time during which the red color was permanent was greatly lengthened. The results are given in Table II.

TABLE II. TIME OF FADING OF FERRIC THIOCYANATE WITH HYDROGEN PEROXIDE PRESENT

Iron P. p. m.	NaCNS, N	H <sub>2</sub> O <sub>2</sub> , M	HCl, N	Time of Fading
0.1	0.2	0.0032	0.01	No fading in 15 minutes
0.1	0.02	0.0037	0.01	No fading in 2.5 hours

Further studies are being made by one of the authors on the rate of ferric thiocyanate fading under definite light conditions.

The fading is believed by the authors to be due to the reduction of the iron and oxidation of the thiocyanate. If that is true, it should be possible to restore full color to a faded iron determination by adding peroxide. To test this hypothesis a solution 0.0028 M in peroxide, the same as used in making curve 2, Figure 1, was allowed to stand several hours. After 4 hours the fading had progressed from 35 scale units to 4. The addition of a second amount of peroxide, equal to the first, restored the original color.

During the past 12 years many hundreds of colorimetric iron determinations have been made in this laboratory using peroxide alone as the oxidant; the results are the same

whether peroxide or permanganate is used, but, because of the fading of the ferric thiocyanate as soon as the permanganate is exhausted, precautions must be taken, when using this procedure, or the results will be low.

### Summary

Hydrogen peroxide is a more satisfactory oxidant for iron than permanganate in the thiocyanate determination of iron. The red color can be made stable for several minutes, depending on the amount of peroxide used, and the faded color may be restored if necessary by the addition of more peroxide. Too much peroxide may cause a yellowish interfering color due to oxidation products of thiocyanate.

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From theses presented by Majel M. MacMasters and Chester L. French for the M.S. degree.

## New Light Sources for Colorimetry

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THE application of a colorimetric method of analysis requires that the system under consideration follow Beer's law, which is theoretically valid only for monochromatic light. However, in practice, it is customary to use continuous or band emission light sources and filter combinations which produce incident illumination of varying degrees of monochromation. In addition to the possibility of major deviations from Beer's law there are other difficulties inherent in such procedures. When permanent standards, differing from the unknown, are used the difference in hue between unknown and standard is greater the broader the spectrum of the incident illumination. In addition, the practical difficulty of determining small changes of transmission in a restricted spectral region in the presence of strong accompanying transmission in other regions (background) becomes greater as the width of the spectrum of the incident light increases.

Although approximations to monochromatic light have been obtained by the use of appropriate filters or combinations of filters, the necessary approximation can often be secured in this way only by the use of exceedingly intense sources (which in the case of tungsten filament lamps generate large amounts of heat) or by the sacrifice of intensity of illumination and therefore of speed and precision.

The lamps described herein were developed in order to secure very high intensity sources of illumination which were relatively cool and whose emission was concentrated in some

restricted spectral region. These permitted the use of thick filters and the attainment of near monochromation without too great a loss of intensity. These lamps were used with the standard Klett-Beaver visual colorimeter, but can be adapted readily to other instruments such as the photoelectric colorimeter, etc.

For the colorimetric determination of sodium chlorophyllins (unpublished work) in aqueous solution use was made of a neon source. The lamp was a spiral of 6-mm. tubing 45 mm. long and 35 mm. in external diameter. With this was used a Corning signal red filter (No. 243) and the standard was a copper sulfate solution (1). The precision attainable (in the determination of concentrations) in this way was approximately 5 parts per thousand for nine readings made in 2 minutes.

For the colorimetric determination of  $\alpha$ -naphthylamine (unpublished work) a green fluorescent lamp was used in conjunction with a Corning Sextant green (No. 401) filter with a pentammino cobaltic chloride solution (1) as the standard. This lamp was in the shape of a doubled "U" and was 11 cm. long and 30 mm. in external diameter. The precision attainable in this case was the same as that given above.

Both these lamps, when in use, were inserted in the place ordinarily occupied by the 25-watt tungsten lamp in the Klett-Beaver colorimeter. Similar lamps, as well as a blue fluorescent lamp, can be obtained in a variety of designs from Claude Neon Lights, Inc., Long Island City, N. Y.

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# Cell and Dropping Electrode for Polarographic Analysis

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IT HAS been common practice in polarographic analysis with the dropping mercury electrode (2) to employ a stationary pool of mercury on the bottom of the cell as the second electrode (usually anode). When this procedure is used, and the current-voltage curves are obtained by means of a polarograph, the observed decomposition voltages and half-wave voltages are in terms of the total applied e. m. f., and hence they depend on the potential of the quiet electrode. Since the potential of the quiet electrode is a variable quantity, depending on the nature and concentration of the foreign salts present in the solution, the values of the half-wave applied e. m. f. are not entirely characteristic of the reducible or oxidizable substances present. The half-wave potentials on a current-voltage curve are only characteristic of the particular electroreducible or electrooxidizable substances present when the values are referred to an external reference electrode of constant known potential. In order to obtain the characteristic half-wave potentials which are required in qualitative polarographic analysis, it is necessary to measure the potential of the quiet electrode against the external reference electrode either at the beginning or the end of the electrolysis and to subtract this value from the half-wave values of the total applied e. m. f. (2).

These extra operations can be eliminated and the characteristic half-wave potentials obtained directly by dispensing with the stationary pool of mercury and employing the reference electrode itself (usually a saturated calomel electrode) as the second electrode of the cell (1, 2, 5). This technique has the further practical advantage of eliminating the extra mercury for the quiet electrode.

The authors have found that the H-cell shown in the diagram is very convenient for practical work. The solution to be analyzed is placed in the left half of the cell and the reference electrode in the right half. Electrolytic connection between the two halves of the cell is made through a sintered-glass diaphragm fused into the middle of the cross arm. To prevent streaming of one solution into the other through the diaphragm, the reference electrode side of the cross arm is filled with a plug of agar containing the same electrolyte used in the reference electrode. When not in use, the left half of the cell is filled with water to prevent the agar plug from drying out and cracking.

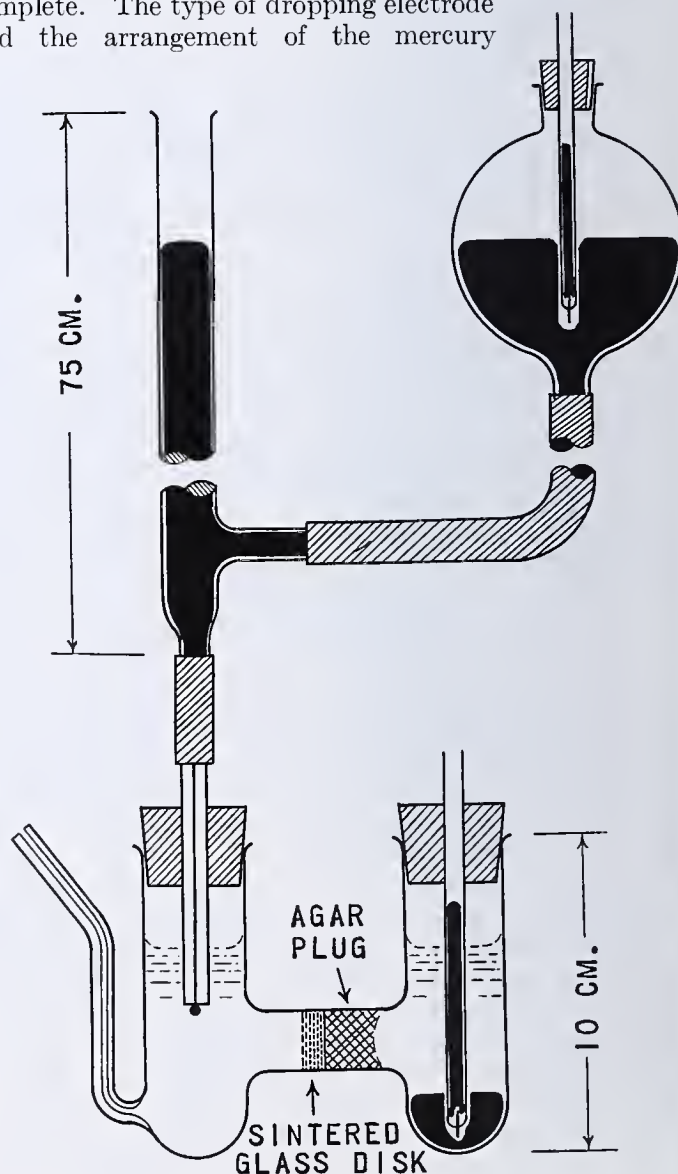
For most practical work a saturated calomel electrode is very convenient as reference electrode, but any other reversible electrode may be used. The area of the reference electrode should be at least 1 sq. cm., or larger, so that it will not become polarized and will retain a constant potential during the electrolysis (2, 6). The reference electrode needs to be renewed only at infrequent intervals.

The authors have also used a silver-silver chloride reference electrode, which in certain respects is handier than a calomel electrode. It remains depolarized during an electrolysis and its potential is as constant and reproducible as that of a calomel electrode. The silver-silver chloride electrode can be prepared either by cementing a piece of silver foil, to which a copper lead wire has been soldered, into the end of a glass tube, or by silver-plating a platinum plate electrode. Its area should be at least 1 sq. cm. or greater. If the silver electrode is to be used as anode in a chloride solution no further treatment is necessary, but if it is to be used as cathode it should be given a coating of silver chloride by polarizing it anodically in a dilute solution of hydrochloric acid.

If the presence of chloride ions interferes in the solution to

be analyzed, a mercury-mercurous sulfate electrode, in saturated potassium sulfate, can be used as the reference electrode (1). The potential of a saturated mercury-mercurous sulfate reference electrode is about +0.6 volt with respect to the normal hydrogen electrode, which is considerably more positive than the potential at which appreciable anodic dissolution of mercury from the dropping electrode takes place (about +0.4 volt *vs.* N. H. E., 2, 7). At the start of the electrolysis when the applied e. m. f. is zero and the dropping electrode is simply short-circuited with a mercury-mercurous sulfate reference electrode, a negative (2) current usually results. This initial negative current will be large when the solution to be analyzed contains halide or other ions which depolarize the dropping electrode (7). In such cases the applied e. m. f. should be increased by a few tenths of a volt to balance out the initial negative current, before connecting the cell to the circuit and recording the current-voltage curve.

The capillary side tube in the left half of the cell is for the introduction of hydrogen or nitrogen to remove air from the solution before electrolysis. During this operation, which requires 10 or 15 minutes, the rubber stopper which carries the dropping electrode is loosened to allow the gas to escape, and is resealed when the removal of air is complete. The type of dropping electrode and the arrangement of the mercury





reservoir shown in the diagram is more convenient than the classical arrangement (2). The dropping electrode proper consists of an 8-cm. length of commercial capillary tubing with a uniform internal diameter of 0.05 mm. (obtainable as "marine barometer tubing" from the Corning Glass Works, Corning, N. Y.). The use of commercial capillary tubing for the dropping electrode has been recommended by Maas (4) and Siebert and Lange (8). The influence on the diffusion current of the geometrical characteristics of the capillary has been discussed in detail by Lingane and Kolthoff (3).

The capillary is connected by a short length of rubber pressure tubing to a vertical tube filled with mercury, which is connected by rubber pressure tubing to the mercury reservoir. The vertical "stand-tube" facilitates the measurement and accurate setting of the pressure on the dropping electrode.

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Silicotungstic Acid Determination of Nicotine

Errors Involved and a New Technique for Steam-Distillation of Nicotine

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THE estimation of nicotine in tobacco and proprietary nicotine preparations by the official method of the Association of Official Agricultural Chemists (1) is a time-consuming and cumbersome procedure, calling for the steam-distillation of 1000 to 1500 ml. of liquid with subsequent aliquoting and precipitation of the nicotine with silicotungstic acid. In view of these facts, the writers have developed a new technique which has proved very convenient. In the course of the work a number of errors inherent in the precipitation of nicotine with silicotungstic acid were encountered. They are of such magnitude and importance in any procedure using silicotungstic acid as the precipitant that it becomes essential to discuss them. Spies (2, 3) has already called attention to the variation in solubility of nicotine silicotungstate with changes in acid concentration of the precipitating medium. Errors from this source are insignificant for any but microdeterminations.

Retention of Reagent by Filter Paper

Experience in this laboratory and elsewhere indicates that an error is introduced in the official method of the A. O. A. C. (1) on account of the retention of silicotungstic acid by filter paper. Experiments designed to determine the magnitude of such error were carried out.

Mixtures containing 100 ml. of water, 3 ml. of hydrochloric acid (1 to 4), and varying amounts of silicotungstic acid reagent (12 per cent) were passed through several makes and grades of filter papers. Each paper was washed with a definite amount of hydrochloric acid (1 to 2000) and burned, and the residue was ignited in a platinum crucible according to the method of the A. O. A. C. (1).

The details of the treatments and the weights of the residues are presented in Table I. Without varying the quantity of wash liquid, and for a given filter paper, the residue obtained varies directly with the quantity of reagent used. Considerable variation is obtained with different papers and also

by varying the amounts of wash solutions. However, under any given set of conditions, the error introduced by retention of the silicotungstic acid reagent by filter paper will be fairly constant. Since only relative amounts of nicotine are considered in the experiments reported below, it was thought not essential to correct for such error. When a highly refined determination of the absolute amount of nicotine present in a given material is desired, it becomes essential to estimate and correct for this error.

Effect of Temperature on Solubility of Precipitate

Low results may also be obtained in the determination of nicotine, because the solubility of nicotine silicotungstate varies directly with temperature. To show this fact, aliquots of a nicotine hydrochloride solution containing approximately 10 mg. of nicotine were all subjected to the following treatment:

Three milliliters of hydrochloric acid (1 to 4) were added to each aliquot and the mixtures were diluted to 100 ml. The nicotine was precipitated with 12 per cent silicotungstic acid solution and allowed to stand at room temperature for about 1 hour until all the precipitates had settled and appeared to be crystalline. Duplicate samples were subjected to the following treatments, after which the precipitates were filtered and washed with hydrochloric acid (1 to 2000); the determination of nicotine

TABLE I. RETENTION OF SILICOTUNGSTIC ACID BY FILTER PAPER

Experiment No.	Filter Paper	Composition of Solution Filtered				Weight of Residue			
		1 + 4 HCl Ml.	H <sub>2</sub> O Ml.	Silico- tungstic acid Ml.	Wash Liquid Ml.	1 Mg.	2 Mg.	3 Mg.	Av. Mg.
1 )	C. S. and S., No. 589, 9-cm., white ribbon	3	100	1	100	0.8	0.8	...	0.8
2 )		3	100	3	100	1.0	1.0	...	1.0
3 )		3	100	5	100	1.5	1.8	...	1.7
4	Munktell, 9-cm., No. 00	3	100	3	100	1.2	1.0	0.6	0.9
5	C. S. and S., No. 589, 9-cm., white ribbon		100	3	100	1.6	1.0	0.8	1.1
6	C. S. and S., No. 589, 9-cm., blue ribbon	3	100	3	100	0.5	0.8	0.7	0.7
7 )	C. S. and S., No. 589, 9-cm., white ribbon	3	100	3	100	0.8	1.0	0.9	0.9
8 )		3	100	3	300	0.6	0.6	0.6	0.6
9 )		3	100	3	500	0.6	0.4	0.5	0.5



was completed as in the official method (1). (1) Samples stood for 8 hours at 0° C. (2) Samples stood for 8 hours at room temperature (about 25° C.). (3) Samples stood for 20 hours at room temperature (about 25° C.). (4) Samples were placed in constant-temperature bath at 35° C. for 8 hours. (5) Samples were placed on steam bath, 80° to 90° C. for 3 hours and filtered hot.

The data in Table II demonstrate that for best results one should allow the nicotine silicotungstate precipitate to stand overnight at 0° to 10° C. before filtering. Better crystallization is effected if the mixture is placed on the steam bath for a short time before holding at the lower temperature.

TABLE II. SOLUBILITY OF NICOTINE SILICOTUNGSTATE

Ex- peri- ment No.	Nico- tine Taken	Volume of Solution	Tempera- ture	Re- agent	Nicotine Found		
	Mg.	Ml.	° C.	Ml.	1 Mg.	2 Mg.	Av. Mg.
1	10	100	0	1	9.87	9.88	9.875
2	10	100	Room	1	9.75	9.83	9.790
3	10	100	Room	1	9.80	9.80	9.800
4	10	100	35	1	9.62	9.53	9.575
5	10	100	80-90	1	8.11	8.22	8.165

### New Technique for Determination of Nicotine

As previously pointed out, dissatisfaction with the apparatus and technique employed in the official method (1) led to the development of a more satisfactory apparatus with corresponding improvements in technique. The apparatus described below, illustrated in Figure 1, is not only time-saving but seems to give more consistent results than does its more cumbersome parent.

**APPARATUS.** The apparatus is a simple steam-distillation outfit which can be constructed, for the most part, from materials at hand in the average chemical laboratory. It consists of a 500-ml. Pyrex Florence flask, *A*, used to generate steam, which is passed through the delivery tube, *B*, under the surface of the liquid in distilling flask, *C*. The steam generator has a three-hole rubber stopper. One hole carries the steam outlet tube, and another a glass stopcock which serves to relieve excess pressure, and through the third passes about 90 cm. (3 feet) of 6-mm. tubing for a pressure gage.

The 50-ml., round-bottomed, Pyrex distilling flask, *C*, is connected through a two-hole rubber stopper and by means of a safety trap, *D*, with a small vertical water condenser, *E*. The delivery tube, *F*, is adjusted in such a way that it dips beneath the surface of the liquid in the 200-ml. Pyrex beaker, used to receive the distillate. Rubber connections are used as shown in Figure 1. Changes in steam pressure can be obtained by adjusting the stopcock opening or by controlling the flame of the Bunsen burner. A small microburner is used to keep the liquid in the distilling flask as low as desired. The entire outfit is assembled on a single ring stand. It can be moved around as desired and does not occupy more than 3.6 sq. meters (2 feet square) of horizontal space.

**PROCEDURE.** It is desirable to use for analysis a sample that contains from 5 to 10 mg. of nicotine, but as little as 2 mg. or less can be determined by this method. Tobacco dusts and other dry preparations of nicotine are usually weighed directly into the distilling flask. In the case of liquid preparations, such as nicotine sulfate solutions of high nicotine content, it is more convenient to weigh the sample in a weighing bottle, transfer it to a suitable volumetric flask, dilute to volume, and pipet a 5-ml. aliquot into the distilling flask. The sample is covered with 2 to 3 ml. of water, and 2 drops of phenolphthalein indicator solution are then added. Sodium hydroxide solution (about 40 per cent) is introduced in slight excess as determined by the indicator. The flask is immediately attached to the outfit and steam is passed into it. A steam pressure of 456 to 608 kg. per sq. meter (1.5 to 2 feet of water) is maintained throughout the run. The beaker used to receive the distillate contains 3 ml. of hydrochloric acid (1 to 4) and about 5 ml. of water. As soon as the distillation proceeds at a smooth rate, the microburner should be used to reduce the volume of liquid in the flask. Distillation is continued for 30 minutes, at the end of which time the liquid in the distilling flask should be reduced almost to dryness and the volume of distillate should preferably not exceed 100 ml. When the distillation is complete, the condenser and delivery tube are washed out and the volume of distillate is adjusted to about 100 ml.

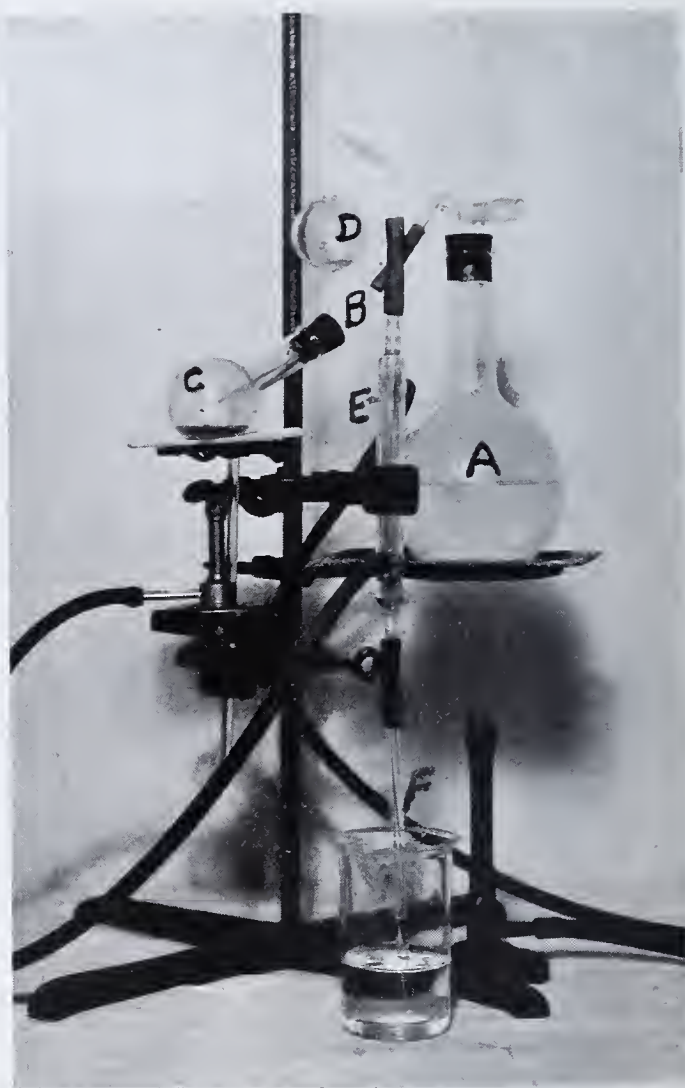


FIGURE 1. APPARATUS

To precipitate the nicotine, 1 ml. of silicotungstic acid (12 per cent solution) is used for every 10 mg. of nicotine or less. After precipitation the covered samples are heated on the steam bath for 15 minutes, cooled slowly to room temperature, and maintained at 0° to 10° C. overnight. The samples are filtered through C. S. and S., No. 589, white ribbon filter paper, and washed with 100 to 200 ml. of hydrochloric acid (1 to 2000). Further determination of the nicotine is made according to the procedures of the A. O. A. C. (1).

TABLE III. ANALYSIS OF LIQUID NICOTINE

Method	No. of Determina- tions	Stock Solu- tion Ml.	Nico- tine Present Mg.	Nicotine Found			%.
				High Mg.	Low Mg.	Av. Mg.	
Direct precipitation	3	5	5.80	5.78	5.77	5.78	99.67
	5	10	11.60	11.65	11.54	11.60	100.00
	5	25	29.00	29.10	29.00	29.04	100.14
New method of distillation	2	5	5.80	5.83	5.83	5.83	100.52
	2	10	11.60	11.63	11.58	11.61	100.08

### Tests of the Procedure

A large number of preliminary experiments were made to determine the length of time necessary for complete distillation of nicotine. No difficulty was experienced in obtaining complete recovery of the nicotine from tobacco powders and proprietary preparations, using a distillation period of 20 minutes. As a safety measure in routine work, it is better to continue the distillation for 30 minutes. Accordingly, 30 minutes has been given as the distillation time in the procedure described above. To analyze a sample of tobacco un-



TABLE IV. DETERMINATION OF NICOTINE IN A COMMERCIAL NICOTINE SULFATE SOLUTION

Method of Analysis	Weight of Sample Grams	(Nicotine guaranteed, 40 per cent)		Alkali Used	Nicotine in Aliquot Mg.	Nicotine Found %
		Aliquot				
		For analysis	For precipitation			
A. O. A. C. (1)	1.0896	...	25/500	NaOH	21.87	40.14
	2.0203	...	10/500	NaOH	16.23	40.17
				NaOH	16.20	40.09
					Av.	40.13
Proposed method	1.0438	5/250	...	NaOH	8.47	40.57
				NaOH	8.47	40.57
				NaOH	8.46	40.53
				Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	8.47	40.57
					8.44	40.43
				Av.	40.53	
Aliquot diluted and precipi- tated directly	1.0438	5/250	...	...	8.54	40.91
					8.54	40.91
					8.53	40.86
					8.56	41.00
					Av.	40.92
Diluted aliquot filtered through 9-cm., C. S. and S., No. 589, white ribbon filter paper before precipitating nicotine	1.0438	5/250	...	...	8.36	40.05
					8.37	40.09
					Av.	40.07

TABLE V. ANALYSES OF COMMERCIAL TOBACCO POWDERS

Sample	No. of Determinations	Method of Analysis	Weight of Sample Grams	Aliquot for Precipitation	Average Nicotine Obtained Mg.	Nicotine Found		
						High %	Low %	Av. %
2	2	A. O. A. C.	5.0	200/500	9.84	0.51	0.47	0.49
	2	Proposed method	0.3		1.52	0.52	0.50	0.51
	2	A. O. A. C.	3.0	200/500	14.29	1.19	1.19	1.19
	2	Proposed method	0.3		3.45	1.15	1.15	1.15
3	2	A. O. A. C.	2.0	200/500	16.20	2.07	1.98	2.03
	2	Proposed method	0.3		5.89	1.97	1.95	1.96
4	2	A. O. A. C.	2.0	100/500	8.21	2.07	2.03	2.05
	2	Proposed method	0.3		6.05	2.02	2.02	2.02

usually rich in nicotine, it would probably be necessary to modify the procedure by decreasing the size of the sample taken for analysis or by increasing the length of time of distillation.

To show that complete recovery of nicotine is obtained by the method described, 1.160 grams of Merck's c. p. nicotine were acidified with a little dilute hydrochloric acid and made to a volume of 1 liter. Aliquots of this stock solution were used for trial determinations, diluting 5-, 10-, and 25-ml. portions to 100 ml., adding 3 ml. of hydrochloric acid (1 to 4), and determining the nicotine with silicotungstic acid solution as previously described. Another series of aliquots was steam-distilled according to the new procedure. The results of these determinations, given in Table III, show that complete recovery of the nicotine was obtained. The high results are probably due to retention of some reagent in the filter paper and some adsorption on the precipitate itself.

In Table IV are recorded the results of several methods of determining nicotine in a sample of commercial nicotine sulfate solution, guaranteed to contain 40 per cent of nicotine. In the first series, the method of the A. O. A. C. was used (1). In the second series, where the new distillation procedure was used, the amount of sodium hydroxide solution was varied from a bare excess to 6 drops in excess. Solid barium hydroxide [Ba(OH)<sub>2</sub>·8H<sub>2</sub>O] was used as the alkali in some cases and was added in amounts varying from 0.2 to 0.5 gram. Two series were run in which aliquots of the diluted sample were analyzed without previous distillation.

The new method of distillation gives slightly higher results than the method of the A. O. A. C. (1) and indicates more complete recovery of nicotine. The high values obtained in the case of direct precipitation indicate the presence of nonvolatile impurities in the material. The low results from the filtered samples indicate that the filter paper retains some nicotine. The authors have obtained other evidence that filter paper adsorbs nicotine under certain conditions.

Four finely ground and air-dried samples of commercial tobacco powder were analyzed by the two methods and the results recorded in Table V. In every case except the first, where the percentage of nicotine was very low, lower but more consistent results were obtained by the new method—just the opposite of what occurred in the analysis of nicotine sulfate solutions. However, the samples used in the A. O. A. C. method contained larger amounts of nicotine than those used in the new method. Table III shows that for direct precipitation, the aliquots containing larger amounts of nicotine gave higher results. These differences can be explained on the assumption that adsorption or occlusion of silicotungstic acid takes place to a much greater extent where large amounts of nicotine are being precipitated.

A series of experiments, using the new apparatus, was carried out to show the effect of using varying amounts of different alkalis—sodium hydroxide and barium hydroxide. The barium hydroxide was weighed to the nearest 10 mg. and the sodium hydroxide was introduced as drops of a strong sodium hydroxide solution, whose strength was previously determined by titration. The tobacco powder employed in these analyses was sample 2 used in the comparison of the two methods of distillation. Table VI shows that excessively large amounts of sodium hydroxide give abnormally high results. This is not true of barium hydroxide and can be explained on the ground that barium hydroxide reaches a limit of solubility and hence much less alkali can be present in solution. It seems probable that the higher results obtained with large excesses of sodium hydroxide are due to something besides nicotine. Whatever may be the cause, for more consistent results the sodium hy-

TABLE VI. EFFECT OF TYPE AND AMOUNT OF ALKALI USED FOR NICOTINE IN TOBACCO POWDERS

Alkali	(Weight of sample, 0.3 gram. Distillation time, 20 minutes)	
	Weight of Alkali Grams	Nicotine Found %
NaOH	0.025	1.12
	0.12	1.13
	0.60	1.15
	1.20	1.24
	2.30	1.24
Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	0.05	1.10
	0.10	1.14
	0.30	1.15
	0.50	1.14
	1.00	1.15
	2.00	1.14



dioxide should be limited to a slight excess over that necessary to produce an alkaline reaction or the use of solid barium hydroxide should be adopted.

### Acknowledgment

The authors are indebted to G. E. R. Hervey for the photograph of the apparatus described in this paper.

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# Thallous Carbonate as an Acidimetric Standard

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HAC and Kámen (2) have suggested the use of thallous carbonate as an acidimetric standard, and Berry (1) has recommended it for standardizations of acids and potassium iodate.

Without knowledge of these two papers, a thorough investigation of thallous carbonate was started with the purpose of establishing its suitability for standardizing acids, and is reported fully elsewhere (3). Some of the observations made command interest in this connection.

With regard to preparation of the salt, the effect of thallous carbonate on glass appears to have escaped notice. It was found that only platinum vessels in recrystallizations will give pure thallous carbonate.

Hac and Kámen have chosen the extraordinary way of providing the absence of copper, lead, and bismuth in the thallous nitrate used for the preparation, but testing the carbonate itself for only sodium and nitric acid. In the case of sodium the sensitivity of the test was not established. Neither they nor Berry gives tests for purity applicable to an unknown sample of the carbonate. Having spectroscopically ascertained the sufficient purity of a sample, tests with and without the addition of the impurity show that the following tests will prove the absence of (<0.01 per cent present) magnesium, calcium, barium, aluminum, iron, manganese, lead, silver, mercury, potassium, sodium, chloride, nitrate, and sulfate.

If 0.5 gram of the substance gives a perfectly clear solution in 5 ml. of hot water, the absence of magnesium, calcium, barium, aluminum, iron, manganese, and lead is indicated.

If 0.5 gram of the substance dissolved in 5 ml. of 2 N sulfuric acid gives neither precipitate nor coloration with hydrogen sulfide the absence of silver and mercury is indicated.

Five grams dissolved in 100 ml. of water are added to 5 ml. of bromine covered with a layer of water, and 25 ml. of 25 per cent ammonia are then slowly added to the mixture. The precipitate of thallous hydroxide is filtered off and washed once with water. The combined filtrates are evaporated to dryness in a platinum crucible and the ammonium salts driven off. The crucible is weighed and the residue extracted with 10 ml. of hot water. The washed and dried crucible is re-weighed. Loss in weight not exceeding 0.5 mg. shows absence of potassium and sodium.

If 0.5 gram in 5 ml. of 2 N nitric acid gives no opalescence with silver nitrate, the absence of chloride is shown.

When 0.5 gram is boiled with 1 ml. of water, cooled, and mixed with an excess of a 1 per cent solution of diphenylamine in concentrated sulfuric acid, no coloration shows absence of nitrate.

To show absence of sulfate, 0.5 gram is dissolved in 3 ml. of 2 N of hydrochloric acid and cooled. The solution is decanted and evaporated to a very small volume (approximately 0.5 ml.). After cooling, the liquid is decanted and one drop of a 5 per cent solution of barium nitrate is added. If no turbidity occurs on standing for 12 hours, no sulfate is present.

It was confirmed that thallous carbonate is stable up to at least 150° C. and nonhygroscopic up to 80 per cent relative humidity and that it does not absorb carbon dioxide from air.

Bromocresol purple was found to be a most suitable indicator, particularly as it gives a perfectly sharp end point in boiling solution.

To give a practical proof of the suitability of thallous carbonate, the normality of hydrochloric acid was established by gravimetric determinations of the chloride, and by standardizations against sodium carbonate. This acid was then used to determine the strength of the different samples of thallous carbonate. The results were:

Gravimetric. N HCl: 0.10066, 0.10070, 0.10075, 0.10071, 0.10073; mean, 0.10071  $\pm$  0.014 per cent  
Standardization against Sodium Carbonate. N HCl: 0.10076, 0.10069, 0.10068, 0.10077; mean, 0.10073  $\pm$  0.024 per cent  
N HCl used as Standard. N = 0.10072 ( $\pm$ 0.02 per cent)

TABLE I. STRENGTH OF THALLOUS CARBONATE

Sample	%	Mean %
Recrystallized in glass vessels. (After taking each sample the bulk was recrystallized.)		
1	99.89, 99.91	99.90
2	99.78, 99.75	99.76
3	100.05, 100.02	100.04
4	99.88, 99.87	99.88
5	99.96, 99.96	99.96
6	100.08, 100.08	100.08
7	100.03, 100.04	100.03
Recrystallized in alkali-resistant glass		
1	99.84, 99.85	99.84
2	100.05, 100.06	100.06
3	99.87, 100.06	99.96
Recrystallized in platinum vessels		
1	99.89, 99.91	99.90
2	100.02, 100.01 100.02, 100.03 99.99, 100.05 100.02, 100.03 99.99	100.02
3	100.01, 100.00 100.01	100.00

A comparison between the figures for gravimetric determinations and standardizations against sodium carbonate and thallous carbonate shows that the individual determinations are in closer agreement with each other (standard deviation 0.017 per cent), whereas greater discrepancies are found among the determinations made gravimetrically (standard deviation 0.03 per cent) or with sodium carbonate (standard deviation 0.04 per cent).

Avoiding glass in the final recrystallizations, thallous carbonate can be readily prepared in a pure state and is then excellently suited as an acidimetric standard.

### Summary

Tests to determine the purity of thallous carbonate as a primary standard in acidimetry have been described.

The results obtained by standardizing hydrochloric acid in various ways agree very closely with those obtained using thallous carbonate recrystallized in platinum.

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# A Device to Prevent Bumping and Promote Boiling

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NUMEROUS devices have been advocated to prevent bumping in distillation, but with possibly one exception (1) none has proved completely dependable.

Most of them function fairly well at the start of a distillation, and as long as boiling is not interrupted. However, temporary removal of the source of heat, the addition of more liquid to the distillation flask, or an increase in pressure, in the case of vacuum distillation, often renders the devices ineffective.

The need for a convenient and dependable device to ensure smooth ebullition is particularly acute in fractional distillation at reduced pressure, where bumping may cause flooding and otherwise seriously disturb the operation of the column.

The "boiling tube," glass beads, broken glass, boiling stones (Carborundum), and a gas stream (particularly for vacuum work) probably find most frequent use because of their simplicity. Glass wool, as proposed by Morton (1), is one of the most effective, but a considerable quantity of the wool is required. Because of the large holdup due to the packing, as shown in Table I, it is impossible to recover small pot residues without extensive dilution by wash solvent.

TABLE I. LIQUID HOLDUP OF GLASS WOOL

Drainage Time Min.	Liquid Retained, <sup>a</sup> No Packing				Liquid Retained, <sup>a</sup> 70 Grams of Glass Wool			
	Tur- pen- tine Cc.	Ethyl alco- hol Cc.	H <sub>2</sub> O Cc.	Pine oil Cc.	Tur- pen- tine Cc.	Ethyl alco- hol Cc.	H <sub>2</sub> O Cc.	Pine oil Cc.
5	2	2	1	4	64	55	100	112
30	1	1	1	2	51	42	86	87
40	1	1	1	2	40	41	86	85
60	..	..	..	..	39	41	86	85
160	..	..	..	..	39	..	..	66
1100 (about 19 hours)	..	..	..	..	..	..	..	57

<sup>a</sup> Cc. retained = cc. added - cc. drained.

In these experiments a measured quantity of liquid was poured into a 2-liter round-bottomed flask, shaken to wet the flask and glass wool thoroughly, and then inverted and drained. The flask was shaken six times during each test to break up pockets of liquid in the glass wool, and thus speed up drainage.

TABLE II. PRACTICAL TESTS WITH PROPOSED DEVICE

Experi- ment No.	Bath for Still Type	Pot Temp. ° C.	Vapors in Still Pot ° C.	Immersion Heater		Watts	Distilla- tion Pres- sure Mm. Hg
				Temp. of Bottom ° C.	Temp. of Top ° C.		
1	Steam	100	88	93	95	7	60
2	Steam	100	88	89	89	0	60
3	Oil	121	88	95	100	7	60
4	Oil	122	88	96	100	16	60
5	Oil	121	91	108	121	18	10
6	Oil	194	153	176	186	20	190

The device described in this paper has been subjected to rigid experimental tests under varying conditions of use. A few experimental runs are recorded in Table II.

## Principal Features

All parts coming in contact with the liquid to be distilled are of glass.

A large promoting surface is provided, consisting of glass thread closely wound around a glass "heater tube." This tube is heated by an easily controlled external means, independent of the heat source for the distillation proper, and activates the glass thread.

The very close contact of the glass thread with the source of heat renders the thread itself comparable to a continuous "hot wire," without introducing hot metal into the distillation liquid.

The glass thread winding extends from the bottom of the distillation flask to a point well above the surface of the liquid being distilled. Boiling is thus promoted over a large surface throughout the depth of the liquid.

The device is compact. The thread does not retain any significant amount of the residual liquid, and can easily be cleaned by washing with solvent.

As the heating medium for the boiling promoter is not in direct contact with the liquid being distilled, any suitable means of supplying heat may be used. When the temperature of the liquid being distilled is not above 90° C., steam may be used very effectively. Oil heated by a rheostat-controlled electric immersion heater made of coiled asbestos-covered wire has been found to serve very well over a wide range of temperatures. In this way a satisfactory temperature differential between the heating medium of the device and the liquid being distilled can be established, and functioning of the device ensured.

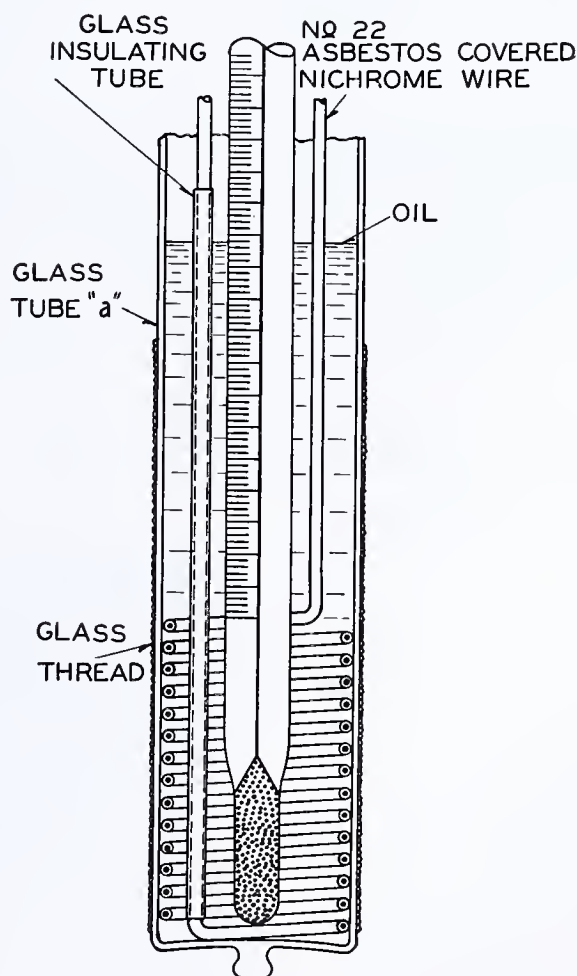


FIGURE 1. HEATER TUBE

This device may also be used in a limited way to provide heat for the distillation. It is best used, however, as a bumping preventer and boiling promoter only, the heat for the distillation proper being provided independently by an oil bath, a steam bath, an electric heater, or other suitable means.

## Construction of Boiling Promoter

The heater tube proper is essentially a wide test tube, the bottom of which is pushed up, and has a small glass button sealed to it to permit fastening the glass thread. This construction, as



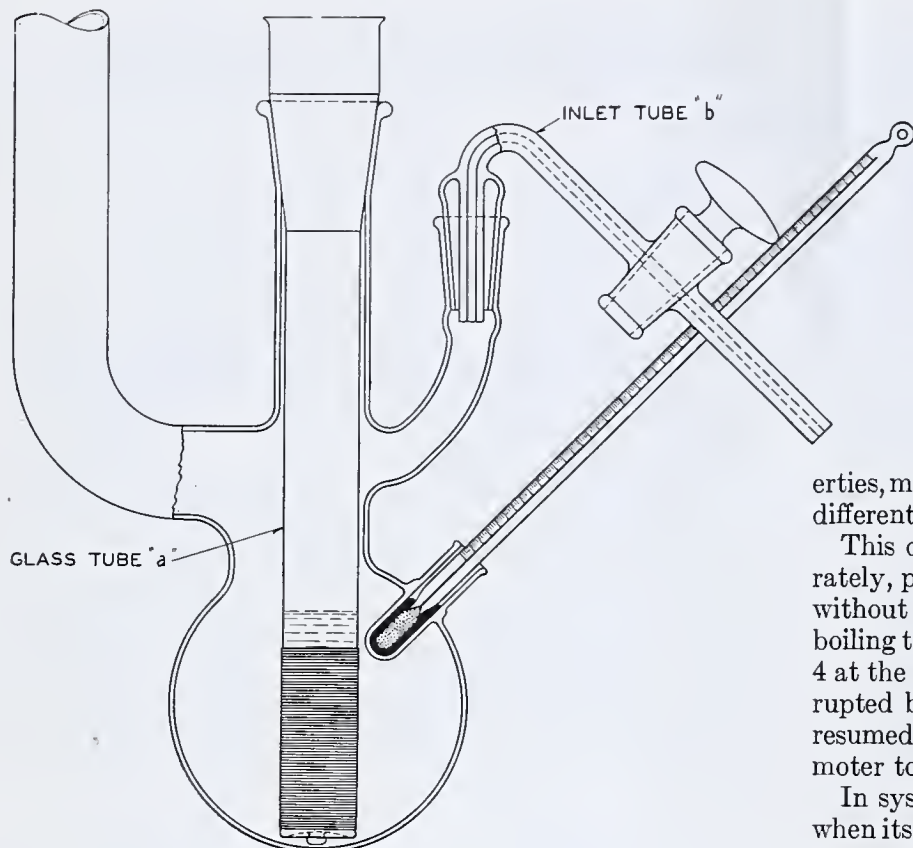


FIGURE 2. APPARATUS

shown in Figure 1, permits winding the glass thread virtually to the very bottom of tube *a*.

The thread, after being fastened to the button, is tightly wound upward with the windings (one thread in thickness) fairly close together, covering the promoter to a height somewhat above that to which the liquid is expected to reach, and the end is securely tied by knotting, looping, and reversing the last few turns.

The heater tube may be inserted into the boiling flask by way of a stopper, or the flask and tube may be equipped with ground-

glass joints, as shown in Figure 2. In that case, careful adjustment of the height of the joint on the flask will have to be made, so that the promoter will just clear the bottom of the flask.

In order to test its effectiveness the device was used not only with a number of liquids, including water, acetone, ether, ethyl alcohol, benzene, methyl chavicol, anethole, fenchyl alcohol, turpentine, terpinolene, and pine oil, in simple distillations at varying pressures, but also as a unit incorporated in a plate column assembly for systematic fractionation. Data on a few typical experiments are recorded in Table II.

As may be seen from experiments 1 and 3, the use of steam, because of its superior heat-transfer properties, makes it possible to operate at a much lower temperature differential between bath and still pot than when oil is used.

This device can also function without being heated separately, provided the distillation is not allowed to stop. Thus, without supplying electric current to the promoter, smooth boiling took place throughout experiment 2, and in experiment 4 at the beginning only. In the latter case, boiling was interrupted by addition of cold turpentine. Smooth boiling was resumed only after supplying sufficient current to the promoter to raise its internal temperatures to 96° and 100° C.

In systematic fractional distillation, the device works best when its temperature is carried sufficiently high so that introduction into the system of additional liquid will not inactivate the promoter but interrupt the boiling only long enough for the added material to be heated to the boiling point. Data were obtained in experiment 5 in a normal systematic fractionation of a high-boiling terpene hydrocarbon, during which the device functioned continuously.

#### Literature Cited

- (1) Morton, "Laboratory Technique in Organic Chemistry," New York, McGraw-Hill Book Co., pp. 104-5, 1938.

## Laboratory Flotation Cell

### A Small Pneumatic Cell of All-Glass Construction

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TAGGART, Taylor, and Ince (3), Oberbillig and Fahrenwald (1), and Prausnitz (2) have described laboratory flotation cells which are designed to give quantitative results. However, the cells of Prausnitz and Taggart, Taylor, and Ince use a large volume of solution and a large sample of mineral. The latter cell, while of excellent design, has a perforated rubber disk and a metal base which make it difficult to clean. The Prausnitz cell is constructed entirely of glass, but both it and the Oberbillig and Fahrenwald cell have flaring tops which cause the froth to collapse during operation, necessitating manual removal of the froth in order to get quantitative results.

The cell described here can be made entirely from glass, and has been designed to work in a setup such as that described by Oberbillig and Fahrenwald (1) for controlling the air flow. Compressed air has been found satisfactory as an air source, each run being made at the same pressure reading on the differential manometer. Each run requires only 50 cc. of solution in the cell, and a 5-gram mineral sample (<200 mesh) gives reproducible results. In order to keep a constant volume in the cell during the run, the solution must be added

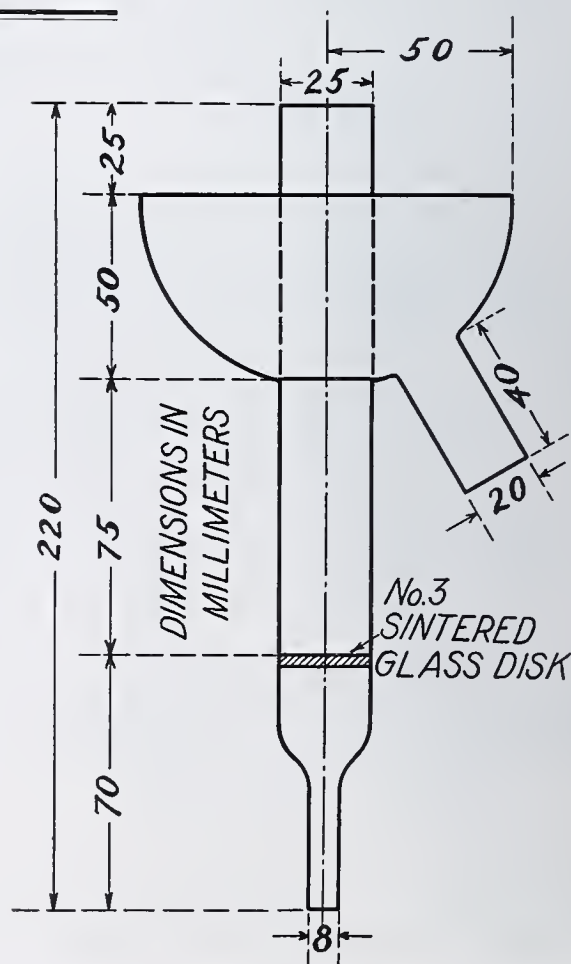


DIAGRAM OF CELL



TABLE I. FLOTATION DATA

Solution	Concn. of Reagent P. p. m.	Galena Grams	Pulp Density %	Recovery %	Galena per Cc. Overflow Gram
Water	...	5.00	10	10.2	0.011
$\alpha$ -Naphthylamine	170	5.00	10	40.0	0.057
	170	10.00	20	22.2	0.092
	170	20.00	40	23.1	0.145
	340	2.00	4	57.8	0.020
	340	5.00	10	60.4	0.061
	340	10.00	20	63.7	0.162
Potassium ethyl xanthate	340	20.00	40	57.8	0.327
	25	5.00	10	75.9	0.118
	25	10.00	20	87.5	0.199
	25	20.00	40	87.6	0.319
	50	5.00	10	82.2	0.117
	50	10.00	20	87.5	0.208
	50	20.00	40	72.0	0.351
	100	5.00	10	84.5	0.094
	100	10.00	20	85.8	0.228
	100	20.00	40	92.7	0.501

let tube is sealed into the trough at the bottom, so that the overflow can be run directly into a filtering crucible for filtering and weighing if desired.

The data given in Table I are taken from unpublished work by Knoll, Leaf, and Baker on the collecting action of  $\alpha$ -naphthylamine on galena. The data on potassium ethyl xanthate are included to show the recovery of mineral when a better collecting agent than  $\alpha$ -naphthylamine is used. The cell described in this paper was used in all cases, although results with the Oberbillig and Fahrenwald and Taggart, Taylor, and Ince cells are comparable.

When solutions which contained no collecting agent were used in the cell, the weight of mineral (galena) recovered depended directly upon the volume of overflow. When solutions containing collecting agents were used in the cell, the percentage recovery of mineral (galena) was independent of the volume of overflow.

Literature Cited

(1) Oberbillig, E., and Fahrenwald, A. W., *Mining J.* (Phoenix, Ariz.), 22, No. 1, 7 (1938).  
(2) Prausnitz, P. H., "Glas- und keramische Filter," p. 129, Leipzig, Akademische Verlagsgesellschaft, 1933.  
(3) Taggart, A. F., Taylor, T. C., and Ince, C. R., *Am. Inst. Mining Met. Engrs., Tech. Pub.* 204, 25 (March, 1929).

A Dipping-Type Conductivity Cell

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THE accompanying illustration shows steps in the manufacture of a conductivity cell, which has been found very useful in measuring the conductivity of water samples in the field and in the laboratory. The cell is made of lucite and is of the commonly used dipping type, with a full-sized opening at

the bottom and several holes at the top to permit circulation of water through the cell. The cell illustrated is used for the measurement of conductivity of water of medium to high conductivity. The cylindrical shield is about 3.25 inches long, 1.25 inches in outside diameter, and 1 inch in inside diameter.

The use of lucite makes it possible to remove the outer shield, which is a convenience in assembling and in cleaning. After the electrodes and lead wires are in place, the holes in the frame that holds the wires are sealed with a cement prepared especially for use with lucite. For field use a cylinder of lucite has been used, instead of a glass cylinder, to contain the sample during the measurement.

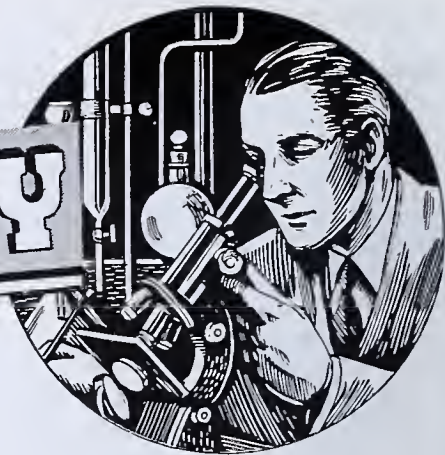
The platinum electrodes and the lead wires were purchased from a manufacturer and the cells were made in the Geological Survey instrument shops.

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STEPS IN THE CONSTRUCTION OF A CONDUCTIVITY CELL





## Determination of Urea

### In Material Used for Filling in Articles of Bedding and Upholstered Furniture

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THE Massachusetts law pertaining to articles of bedding and upholstered furniture is administered by the Massachusetts Department of Public Health. This law provides in part that each article of bedding or of upholstered furniture shall be plainly marked with a statement in English of the kind of material used for filling, the name of the manufacturer or vendor, and, if the material has previously been used, the words "second hand." "Previously been used" means used as a part or portion of another manufactured article, or for any other purpose. A 1936 amendment permits the use of clippings of new cloth under the name of new material in the manufacture of upholstered furniture.

In early attempts to enforce this law it was necessary to rely upon experts from the waste trades for extremely unsatisfactory testimony regarding the secondhand nature of the material used for filling. The last such expert used by the department stated on the witness stand that very obviously secondhand material in his opinion could well be characterized as new within the understanding of the trade. The defendant was found not guilty, and the judge expressed regret that he was obliged to rely on the testimony of the expert for his decision.

The department then used an ultraviolet lamp to differentiate between new and secondhand material. The method (9) is simple and rapid, as it consists of examining the materials in a dark room by strong ultraviolet light (3130 to 4045 Å.), and noting the color and intensity of the fluorescence. In the case of new raw or bleached cotton the fluorescence ranges from red-violet to blue-violet. In the case of cotton impregnated with urine or perspiration, it is pale blue if the impregnation is fresh and ivory if the impregnation is at least a month old. The reliability of this method depends on ability to judge colors and shades of color and to interpret their significance. Colors and shades of color are difficult to describe; for that reason the chemist should familiarize himself, by actual examination, with known new and secondhand materials which he should keep on hand for comparison with unknown materials being tested. This method is best suited for the examination of raw or bleached cotton, and is obviously useless for dyed materials and for animal fibers.

However, more satisfactory methods were needed. It occurred to one of the authors (Racicot) in 1934 that it might be possible to detect the presence of urea in material that had been in contact with the human body long enough to absorb

minute quantities of urine or perspiration, and by such a method to prove that the material had been previously used. After considerable research work, qualitative methods for urea and creatinine were adopted and used successfully in a contested case where the defendant introduced expert testimony.

In July, 1935, there appeared an article (10) by Yee and Davis upon the microdetermination of urea. This method was immediately studied and modified considerably in order to utilize apparatus used in the determination of ammonia in eggs, meat, and meat products (2). This modified method has been used with success to date.

In September, 1935, the authors' attention was brought to the method of Moskowitz, Landes, and Himmelfarb (3) for distinguishing between new and secondhand cotton filling materials. This article listed analyses of thirty-six samples of so-called new cotton wastes with a urea content ranging from 0 to 9 mg. per 100 grams of material—on the average considerably higher than the values found by the authors of the present article in waste material which they had reason to believe was not secondhand. These high figures, as well as the presence of small amounts of urea in the new waste materials in somewhat constant concentration, were attributed to the presence of urease, which is a constituent of certain seeds.

In order to ascertain whether cottonseed or raw cotton contains urea, whether cottonseed contains urease, and whether the reaction under ordinary conditions is reversible, the following experiments were made with cottonseed, linters, and raw cotton.

EXPERIMENT 1. Ten grams of cottonseed were soaked for 2 hours in water at a temperature of about 35° C. The extract was filtered from the seeds, the seeds were washed, and the filtrate was made up to 100 cc. Five cubic centimeters of this extract were tested for the presence of urea by the Nicloux and Welter microgravimetric method (4), which gives reliable results for quantitative determination as small as 0.05 mg., or if used as a qualitative test will detect the presence of one part of urea per million. No urea was found in this solution.

EXPERIMENT 2. Ten grams of cottonseed were taken, soaked in warm water, and filtered, and the filtrate was made up to 100 cc. Two aliquots of 20 cc. each were then taken; to 1 aliquot were added 100 mg. of urease, and the mixture was fermented at 50° C. for 15 minutes. A blank containing the urease in distilled water was similarly treated. All three were then subjected to the Folin aerometric method (2) for the determination of ammonia,



using Nessler solution as the reagent. The blank contained 0.074 mg. of ammonia, the unfermented extract contained 4.69 mg., and the fermented extract contained 4.76 mg. Subtracting the blank from the fermented extract result gives a figure identical with that of the unfermented extract. Consequently no urea was present in the cottonseed.

Several samples of raw cotton of known purity were examined by this method, and no urea was found.

The following experiments were undertaken to determine whether or not cottonseed contains urease.

**EXPERIMENT 1.** Five grams of cottonseed were placed in a wide-mouthed flask, and 20 cc. of urea solution containing 18 mg. of urea were added, with sufficient distilled water to cover the seeds. The material was allowed to stand overnight, filtered, and washed, and the filtrate was made up to a volume of 100 cc. Twenty cubic centimeters of the urea solution containing 18 mg. of urea were placed in a 100-cc. volumetric flask, and the solution was made up to the mark with distilled water. A 5-cc. aliquot of each solution was taken, and urea determinations were made upon each by the Nicloux and Welter method. The solution containing the cottonseed extract and urea was found to contain 0.914 mg. of urea. The solution containing the urea alone was found to contain 0.900 mg. of urea.

The water extract was filtered and treated with acetone according to Van Slyke's method (6) for extracting urease from the jack bean. The residue obtained by evaporation of the acetone extract was dissolved in water, urea was added, and the solution was then incubated at 50° C. for 15 minutes in a flask. A few drops of methyl orange indicator were added; the solution remained neutral after 24 hours, showing the absence of free ammonia. From this experiment we must conclude that the cottonseed was free from urease.

The following experiments were undertaken to determine whether or not the reaction of urease or urea is reversible. Urease will convert urea into ammonium carbonate, and this when warmed will split into water, ammonia, and carbon dioxide.

In one experiment three wide-mouthed flasks were used. To one flask were added 5 grams of cottonseed covered with linters and impregnated with 100 mg. of urease powder; to the second flask, 5 grams of clean absorbent cotton impregnated with 100 mg. of urease powder; and to the third flask, 100 mg. of urease powder. To each flask was added some moistened ammonium carbonate. The flasks were stoppered and allowed to stand at

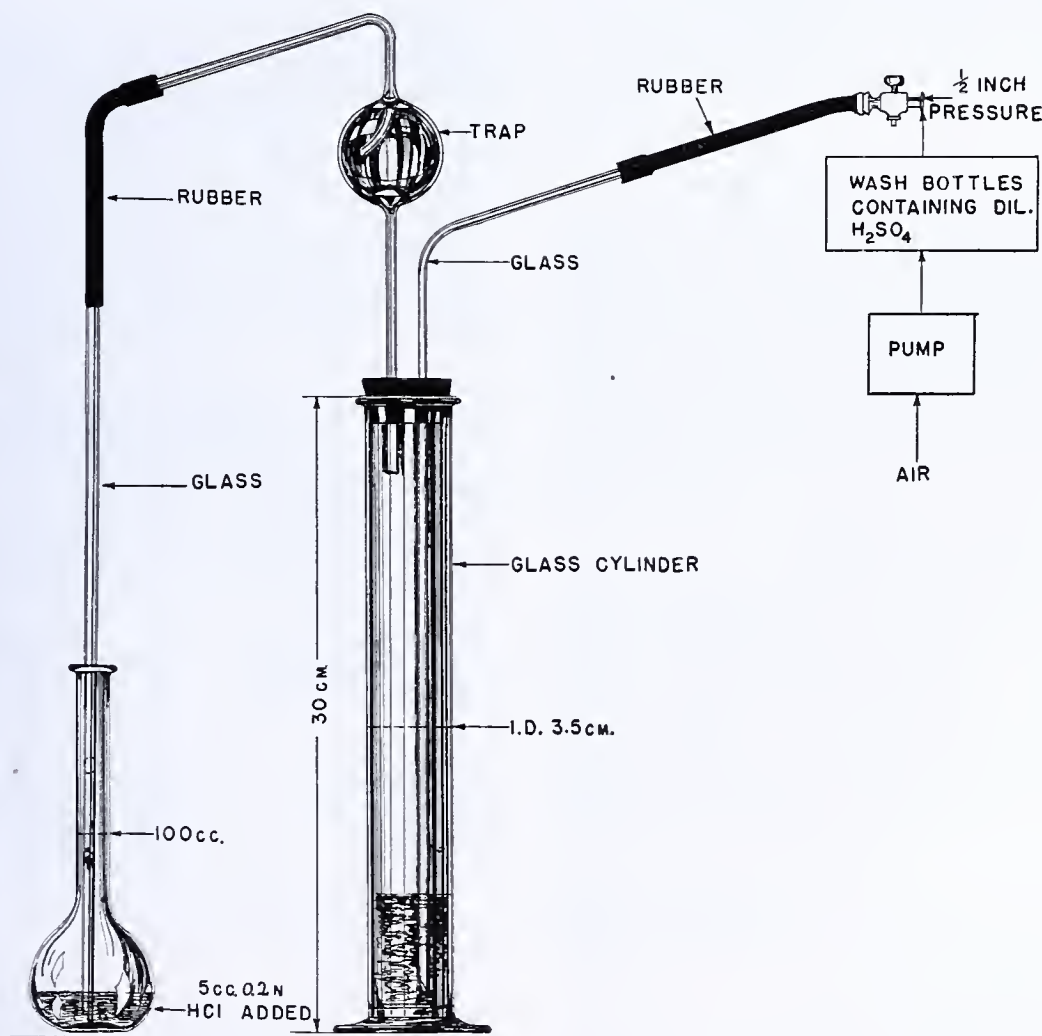


FIGURE 1. AERATION APPARATUS

If the cottonseed contained urease, part of the urea should have been hydrolyzed to ammonia and carbon dioxide, and, therefore, the urea in the solution containing the cottonseed extract should have been less instead of more than in the urea solution alone. From this experiment we must assume that there was no urease in the cottonseed at the authors' disposal.

**EXPERIMENT 2.** The cottonseed used in experiment 1 was unbroken and was covered with so-called linters. Urease when found in seeds containing this material is in the cotyledons and not in the hulls. In order to ascertain whether urease may have been present in the cotyledons, a 100-gram sample of the cottonseed was ground to a fine meal, and this meal was then extracted

room temperature overnight, and the contents were then analyzed for urea. No urea was found in any flask, in spite of the fact that the urease was exposed for several hours in an atmosphere saturated with ammonia, carbon dioxide, and water, which naturally would be most favorable conditions for reversing the reaction.

A large piece of filter paper was impregnated with 100 mg. of urease and hung up in the laboratory for 30 days. The atmosphere of the laboratory should contain at least as much ammonia, carbon dioxide, and water as is found in a cotton storage warehouse. After 30 days this filter paper was analyzed for urea; no urea was found.



TABLE I. ANALYSES OF TRADE WASTE OBTAINED FROM MATTRESS FACTORIES AND FROM TRADE WASTE DEALERS

Trade Designation	Ash %	Oil %	Ammonia Mg./100 grams	Urea	Fluorescence in Ultraviolet Light
Picker	5.52	2.3	20.40	0.74	Violet, oil spots, yellow spots
Picker and fly	3.30	0.5	7.81	-1.18	Violet, dirty
	3.12	0.3	6.17	-0.83	Violet, oil spots
	5.14	1.2	10.10	-0.79	Violet, dirty
	3.32	0.8	8.33	-0.46	Violet, oil spots
	3.24	2.0	10.75	-0.11	Violet, oil spots
	2.86	0.5	4.65	+0.05	Violet, oil spots
	2.35	0.5	6.58	0.16	Violet
	3.89	0.7	7.40	0.32	Violet, few oil spots
	3.47	2.9	1.97	0.40	Violet, oil spots, dirty
	2.83	0.7	10.10	0.58	Violet, dirty
	3.00	0.8	5.26	1.58	Violet, dirty
Fly	3.84	0.8	6.94	1.48	Violet
	3.40	1.5	13.88	1.67	Violet, oil spots, dirty
Cotton felt	1.98	0.7	4.07	1.48	Violet
Garnetted felt	2.02	0.7	6.19	-1.04	Violet, oil spots
	1.87	0.4	6.57	-0.35	Reddish violet
	2.31	1.3	5.17	+0.79	Violet
1st grade	1.78	0.4	5.19	-0.09	Violet
	1.46	0.4	3.63	+0.84	Violet
2nd grade	2.05	1.0	5.19	0.70	Violet
	1.65	0.7	4.67	1.69	Violet
China garnetted felt	0.91	0.5	3.40	1.14	Violet
	0.94	0.8	4.73	1.99	Violet
Rollers	2.80	2.2	6.52	-0.81	Violet, oil spots
Strip	3.69	0.6	5.19	+1.37	Violet, oil spots
Av.	2.80	1.08	6.96	0.44	

In two contested cases in Massachusetts, Himmelfarb (co-author, 3) testified as an expert for the defendants. George L. Drury, the inspector handling the cases, cross-examined Mr. Himmelfarb with particular reference to the authenticity of the alleged new-material samples which were the basis of his publication. It appeared from this testimony that the material was obtained from the trade waste dealers as new and was accepted as such without further investigation. Experience has shown that the trade is likely in some instances to submit material far different from what is expected.

### Method of Analysis

The method of analysis is based on the enzymatic action of urease on urea and the subsequent quantitative determination of ammonia, one of the products of the reaction. Since urea in bedding and upholstering materials indicates the presence of urine or perspiration, which give off free ammonia in alkaline solutions, this free ammonia must be determined and the quantity found subtracted from the ammonia found in the urease fermented portion; the difference is urea ammonia, which is computed to urea.

**REAGENTS.** Hydrochloric acid, 0.2 N. Urease, 100-mg. tablets (buffered). Defoaming agent, Racicot and Ferguson (5) octyl alcohol, paraffin, and mineral oil. Borax solution, saturated at room temperature. Nessler's reagent. Ammonium sulfate solution, 1 or 0.5 mg. of nitrogen per 100 cc.

Procure the purest ammonium salt available, dissolve it in water, add sufficient saturated sodium carbonate, and, by a strong current of air, aspirate it into sulfuric acid solution. Precipitate the resulting ammonium sulfate with alcohol, filter, wash with diluted alcohol, and dry. By this method impurities which may affect the Nessler solution are removed (1).

**APPARATUS.** The apparatus is shown diagrammatically in Figure 1. It consists of 2 aeration glass cylinders and 2 receiving flasks (100-cc. volumetric flasks containing 5 cc. of 0.2 N hydrochloric acid diluted with 50 cc. of distilled water), the inlet tubes of the aeration cylinders being connected to the wash bottles and air pump. The air pump and the wash bottles containing dilute sulfuric acid are standard equipment.

**PROCEDURE.** Weigh 10 grams of the material and place in a 400-cc. beaker; add about 60 cc. of boiling distilled water, and knead with a heavy glass rod until thoroughly wetted. Allow to stand for 1 hour, transfer to a Büchner funnel, filter, and wash by suction. Transfer the filtrate to a 100-cc. volumetric flask,

cool to room temperature, and make to volume with distilled water.

Set up the apparatus, unstopper the cylinders, place a 100-mg. tablet of urease in one of the aeration cylinders, add about 5 cc. of distilled water, and dissolve. Then, from the 100-cc. volumetric flask containing the extract of 10 grams of the material, pipet accurately two 20-cc. aliquots, one in each aeration cylinder. Restopper the cylinders and, without disconnecting, lift the cylinder containing urease and stand it in a beaker containing water which has been warmed to 45° C. Mix the solution by gently shaking, and allow to stand for 15 minutes, shaking occasionally. A fermentation of 15 minutes at 40° C. ensures complete decomposition of urea.

At the end of this period remove the water bath, allow the cylinder to cool to room temperature, make the solutions in the two cylinders equal in volume, add defoaming agent and 20 cc. of saturated borax solution to each cylinder, stopper tightly, and start the air pump. Adjust the flow of air to at least 10 bubbles per second, and aspirate for 2 hours. Then remove the receiving flasks, add 25 cc. of diluted Nessler solution (5 cc. plus 20 cc. of water) to each flask, dilute to the mark, and compare with a standard solution of ammonium sulfate, using a colorimeter as in the Folin method for the determination of ammonia (2). An analysis should be made on a urease tablet and a correction made if necessary. Any increase in ammonia in the solution to which urease is added is due to urea. A blank determination on the reagents is also advisable.

Table I gives the results of the examination of material collected from mattress factories and from wholesale dealers in mill wastes and shows the results of the ultraviolet light examination, as well as the ash, oil, and urea content. The ash was determined because of an attempt to use as new material some imported wastes heavily loaded with clay and also containing considerable oil, presumably to cause the clay to stick to the fiber. The oil was also determined, to furnish information for the differentiation between normal new waste material and wastes heavily impregnated with oil, known in the trade as "oily mill sweepings."

TABLE II. ANALYSES OF WASTES FROM A COTTON MILL AND FROM LOWELL TEXTILE SCHOOL

Sample No.	Character of Material	Ammonia Mg./100 grams	Urea	Fluorescence in Ultraviolet Light
A <sup>a</sup>	Droppings (opener room)	12.90	0.42	Violet plus dirt and chaff
B <sup>a</sup>	Picker	8.47	-0.05	Violet plus white tufts; latter violet when shredded
C <sup>a</sup>	Card droppings	7.04	0.00	Violet
D <sup>a</sup>	Comber waste	1.92	0.12	Violet
E <sup>b</sup>	Undusted picker	8.19	0.61	Violet plus white tufts; latter violet when shredded
F <sup>b</sup>	Undusted fly (moats and fly)	3.92	-0.76	Violet
G <sup>b</sup>	Fly	10.52	-0.19	Violet
H <sup>b</sup>	Flat strips	4.65	-0.79	Violet
I <sup>b</sup>	Rollers	8.84	-0.11	Violet
J <sup>b</sup>	Comber	1.62	-0.13	Violet
Av.		6.81	-0.09	

<sup>a</sup> From a cotton mill.

<sup>b</sup> From Lowell Textile School.

The department obtained a number of samples of mill wastes, which were classified as new material after careful examination by Ralph Cooper, inspector of the department, who was formerly employed in the manufacture of upholstered furniture. Ultraviolet light confirmed this opinion in each instance. Subsequently a large cotton mill was visited and samples of cotton wastes were obtained from the machines used in manufacturing cotton fabrics from the raw cotton in the bale to the finished product. Table II shows the results of the examination of samples collected in the mills and in the Lowell Textile School during the process of manufacture.

In considering the results of these analyses, it will be noted that some wastes gave a negative urea content. It was first thought that this was due to eyestrain in reading the



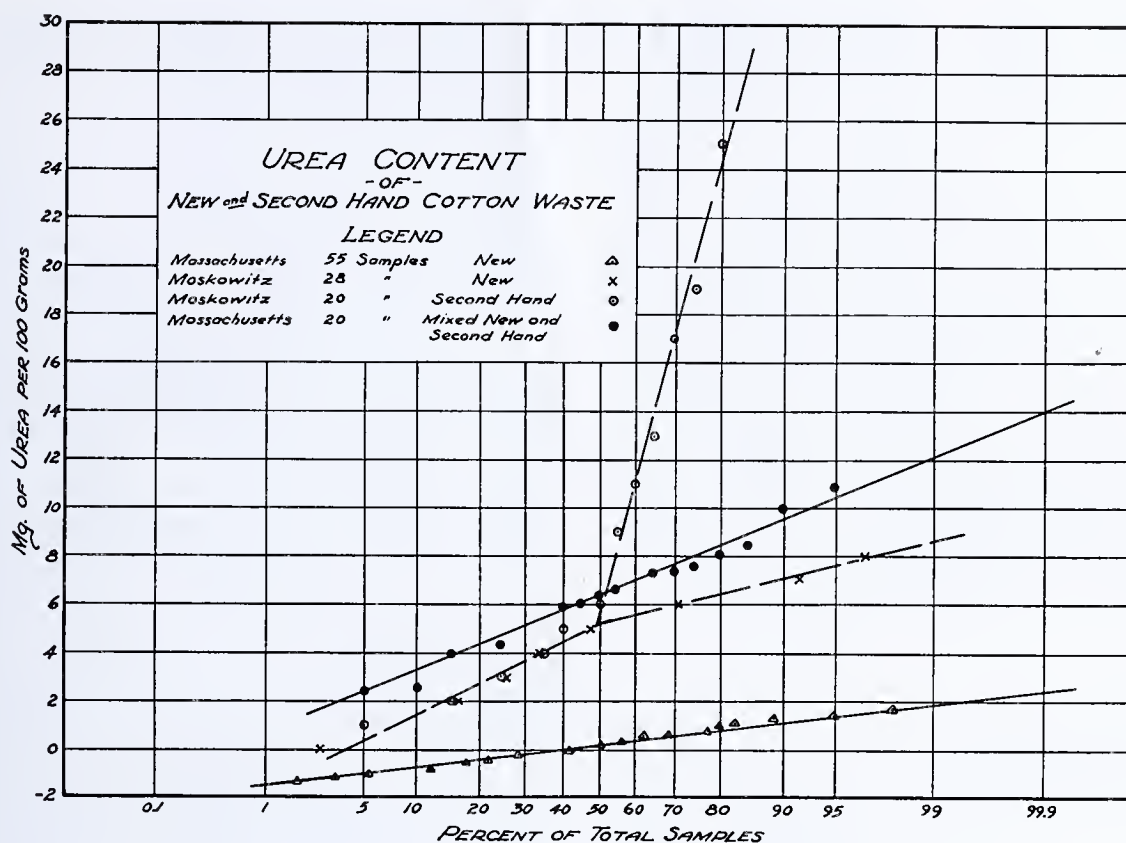


FIGURE 2

colorimeter, but similar results were obtained on additional samples, using a photoelectric colorimeter during examination.

Each urea figure is calculated from the difference between two ammonia microdeterminations, one of which is corrected by a blank determination on the urease. If the material contains little or no urea, a slight error in the determination of ammonia in either solution could readily result in a negative value for urea, particularly if, as in this instance, each analytical figure is from one determination and does not represent the average of two or more check analyses. The standard ammonia solution used for comparison with the unknown was selected to give most accurate results when analyzing material of fairly high ammonia concentration. The difference between the intensity of the color of the sample and the standard is to some extent responsible for the negative urea values reported.

Figure 2 shows certain urea figures plotted on arithmetic probability scales. This type of paper, known as Hazen and Whipple's probability paper, was first devised by Allen Hazen in 1913 (8). The percentage scale of this paper is so spaced that any set of figures which follows the natural law of probability will plot in a straight line. The 50 per cent line of this scale is placed in the middle of the percentage scale. Subsequently Whipple (7) showed that when the series did not plot as a straight line, as is usual with figures involving bacterial counts, it would frequently do so if the other scale of the paper were changed from arithmetic to logarithmic. Figures for plotting on this type of paper are arranged as a summation series in ascending order and from this arrangement a summation percentage series is calculated. If the arithmetic average of this series closely approximates the 50 per cent value, the figures are plotted upon arithmetic probability paper, but if this average exceeds to any extent the 50 per cent value, logarithmic probability paper is used. The authors' 55 samples of new material plot in a straight line, as do those of mixtures of new and secondhand material, such mixtures being identified by the ultraviolet fluorescence. Each of these series, therefore, follows the natural law of probability.

The figures for new material published by Moskowitz *et al.* are different, as the urea content is on the average much higher than that of samples collected by the authors, and the figures do not plot in a straight line on this paper. The lines representing the Moskowitz analyses are both broken at about the 50 per cent mark, and each plots as two probability series; lines for the lower 30 per cent of each series are almost identical. If, as the testimony of Himmelfarb indicates, the authenticity of the wastes was not carefully investigated, the waste dealers may have submitted as new some mixtures containing secondhand material; this will explain the discrepancy in the results, assuming that the method used for analysis was accurate.

The authors' figures indicate that by their method there is not one chance in ten thousand that the urea content of new wastes will exceed 2.8 mg. per 100 grams. By ultraviolet light examination, together with a determination of the urea content, the presence of secondhand material in cotton wastes can usually be detected, unless such secondhand material has been thoroughly scrubbed and washed, in which case it is substantially, if not legally, the same as new material and would probably cost more.

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# Electric Melting Point Microapparatus

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VARIOUS types of electric melting point equipment to be used with the microscope have been reported using a variety of heating arrangements, recording devices, and constructional materials. Pieces of apparatus employing the application of the thermocouple have been designed by Oberhoffer (10), Niethammer (9), and Wallace and Willard (11). Laboratory thermometers have been used by Cram (5), Clevenger (3), and Chamot and Mason (2). Other unique variations have been used by Jentsch (8), Cottrell (4), and Admur and Hjort (1). Dannenberg (6), Eitel and Lange (7), and Walton (12) have perfected special types of microscopic hot-stage equipment. At least two types of microapparatus, those of G. Klein and Fisher-Johns, are available commercially (Fisher Scientific Co., Pittsburgh, Penna).

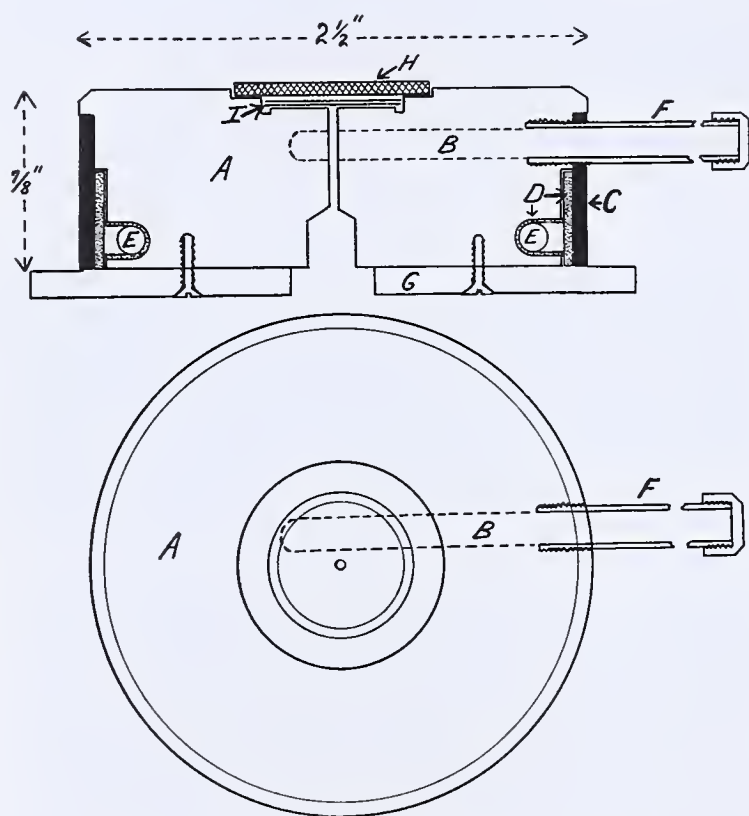


FIGURE 1. VERTICAL AND HORIZONTAL DIAGRAMS

The author's apparatus consists essentially of a solid aluminum block that has been carefully shaped or turned on a lathe, is heated by means of resistance wire, and carries a thermometer well. Figure 1 is drawn to scale.

The aluminum block, A, is cylindrical in shape and measures 0.875 by 2.5 inches. If a block of aluminum of this size is not available, smaller pieces may be melted in a muffle furnace, cast into a slightly larger block, and turned down on a lathe to the correct size. A series of concentric depressions is made on the top surface of the block, of a size to admit two circular microscope cover glasses, I, and immediately above a still larger circular piece of glass, H. H can be readily cut to any desired size by spinning a suitable sized cork borer or piece of brass pipe on a piece of clear glass, using a suspension of silicon carbide or emery dust in water for cutting purposes. A small depression at the outer edge just below I aids greatly in the removal of the cover glasses when the apparatus is in use. Some time can be saved and difficulty avoided if H and I are first prepared and then the depressions are cut to a suitable size and depth. A small hole is drilled straight through the center of the block from the bottom of these depressions and is enlarged somewhat at the base. This opening serves to illuminate the sample when melting point determinations are being made.

A should slip snugly into a brass or copper ring, C, which covers and protects the heating element, E, below. A small depression is cut near the base and completely around A, and is lined with asbestos paper, D, for electrical insulation. Three feet of B. & S. gage No. 22 chromel wire, E, with approximately 3 ohms resistance, is then wound into a small spiral coil which is embedded in the insulated depression and drawn completely around A. The ends of the wire are led through holes in C and fastened to suitable electrical binding posts. A layer of asbestos paper, D, is slipped between E and C for electrical and thermal insulating purposes. Provision is made for D in A, as illustrated. If an overhanging flange is left on A, resting upon the upper edge of C, the whole can be more securely fastened in place. The completed block, A, rests upon an asbestos slate Transite base, G, and all are held securely in place with two small screws as illustrated.

The thermometer well, B, in A is drilled horizontally and as near the top surface as possible. It should extend slightly beyond the center and enough to one side just to clear the small hole through the center of the block (Figure 1). The thermometer should be protected with an armor, F, securely screwed into the metallic block. The lag in the thermometer is much less if the bulb is packed in aluminum filings when the apparatus is assembled.

A convenient wiring arrangement is shown in Figure 2. The apparatus, A, is connected in series with a switch, K, and variable resistance, M, of approximately 50 ohms' resistance. A 10-watt light bulb, L, is connected across the 110-volt leads, with switch J in series, to be used for illuminating the sample. Convenient switches, binding posts, and similar items can be secured at radio supply stores.

Figure 3 illustrates a compact arrangement, which includes the microapparatus, source of light, and resistance. The variable

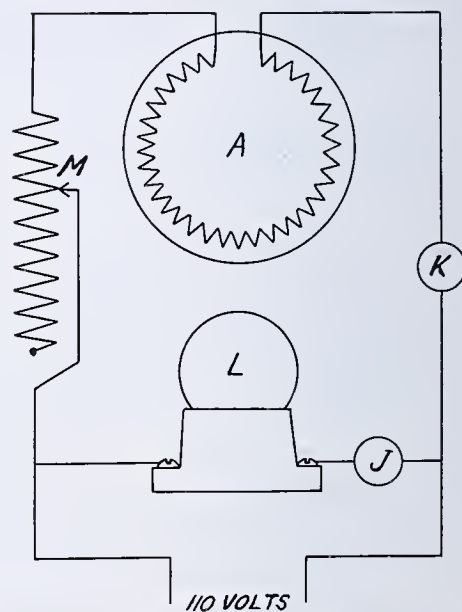


FIGURE 2. WIRING OF APPARATUS

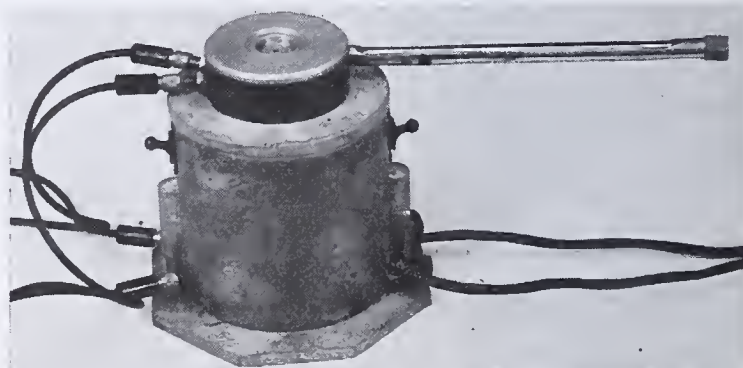


FIGURE 3. APPARATUS, LIGHT SOURCE, AND VARIABLE RESISTANCE



resistance is mounted within the metal container. Necessary insulated electrical leads are provided through the walls. The 10-watt bulb is mounted in the center, immediately below the opening for illuminating the sample. However, the leads from the variable resistance to the aluminum block should be of sufficient length to permit the transfer of the block to the stage of any compound microscope. Otherwise the samples may be observed with the naked eye or by use of a tripod magnifier.

When a melting point is to be taken a small crystal of the unknown is placed between the microscope cover glasses, *I*, and above the small opening provided for illumination. *H* is then placed in position. The temperature is raised and controlled by the amount of current provided through *M*. The sample should be illuminated by direct light from *L* or by reflected light where the compound microscope is used.

Not only melting points but any tendency for the unknown to soften or sublime can be observed under these conditions. Frequently the presence of impurities can be detected by different melting points or other unusual be-

havior, not ordinarily observable by other melting point methods. Any discrepancy from true melting points due to faulty calibration of the thermometer or thermal losses at high temperatures can easily be corrected by checking melting points of known compounds over the temperature range involved.

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# Carbon and Hydrogen Determinations

## Effect of Pressures on Lessening Combustion and Sweeping Times

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THERE has been great need for lessening the time required for microdeterminations of carbon and hydrogen. Authors of methods for microanalysis at best suggest from 45 to 50 minutes as combined combustion and sweeping times. Those who have had experience with combustions with polyhalogen compounds, compounds containing sulfur or nitrogen, or combinations of all three, know that extreme care must be taken not to get too high results for carbon. This leads to an examination of the manner of filling the combustion tube, since its function is to remove the unwanted halogens, sulfur, and nitrogen (if it is burned to oxide). Inasmuch as the trend is to semimicroanalysis, using samples on the order of three to seven times the maximum size of microsamples (when sufficient material is available), it was felt that a tube of larger cross section would be advantageous. Conditions which would speed up semimicrodeterminations should also hold true for microsamples.

Initially, with the set described (1), a tube of Pregl dimensions was used and filled in the conventional manner. Samples from 12 to 35 mg. were burned. With 20 to 25 minutes arbitrarily set as combined combustion and sweeping times, the results were much too poor. Compounds containing nothing but carbon and hydrogen, or carbon, hydrogen, and oxygen gave closer results than those containing in addition halogen, sulfur, or nitrogen. The smaller tube was soon abandoned in favor of a larger tube of 11- to 12-mm. bore.

It can be argued that a tube of wider bore will contain more filling, permit better removal of the halogen, sulfur, etc., and last longer. The filling of the tube differs in two respects from that previously described (1): The precipitated silver is supported on short-fiber asbestos, and the tube is packed rather tightly. This tight packing enables combustions to take place under pressure. The exit ends of the capillaries of the absorption tubes are further constricted to enable absorptions to take place under pressure. The pressure in the combustion tube varies with the bubble rate, but is constant for a fixed bubble rate. For example, with the particular tube the author is now using, at 100 bubbles per minute the pressure is about 5 cm. of mercury (1 pound),

and at 180 bubbles per minute, about 10 cm. (2.0 pounds). These two figures are given because combustions take place at 100 bubbles per minute, and sweeping at 180 bubbles per minute. As yet the author has found no sample up to 35 mg. that is not completely oxidized and absorbed within the time limits set. No more than 225 cc. of oxygen are required for combustion and sweeping of any sample up to 35 mg. (The pressure figures throughout this paper are approximate.)

A simple device enables one to measure the pressure in the combustion tube. With the pressure chamber (which has displaced the glass gasometer described in the previous article, 1) set to 250 cm. of mercury (50 pounds), and the set diaphragm delivering the oxygen at a head of 35 cm. (7 pounds), the delivery needle valve is adjusted to 100 bubbles per minute.

At intervals, while filling the combustion tube, the tube is checked for pressure head by inserting a three-way stopcock into the open end of the combustion tube by means of a rubber stopper. To the opposite end of the stopcock is joined an open mercury manometer. The exit end of the combustion tube is left open. The set soon comes to equilibrium and the pressure rise is noted in the manometer. The short-fiber asbestos mixed with precipitated silver and the lead peroxide supported on short-fiber asbestos are tamped until the desired pressure head is reached. The third opening of the three-way stopcock is used for regulating the pressure head in the absorption tubes. The absorption tube is connected by means of rubber tubing to the arm of the stopcock, the end of the combustion tube is plugged, and the exit ends of the capillaries of the absorption tubes are constricted until they show a pressure head of approximately 1.25 to 1.8 cm. of mercury (0.25 to 0.375 pound).

Even though pressure plugs are included in the standard Pregl set, the pressures are below those cited in this paper. Moreover, it is apparent that the absorption tubes are always under a slight vacuum due to the pull of the Mariotte bottle. This suggests the necessity for slow combustion and absorption times. Under pressure absorption is more complete than under slight vacuum.

The reproducibility of the results is indicated by Table I. Since an analytical balance of sensitivity 40 was used, the discrepancies in the last two places of decimals might be due to the inaccuracy of the balance.



With the simplification of procedure, impetus should be given to the teaching of micro- and semimicrodeterminations. All the troublesome and involved techniques are a distinct deterrent when time is a factor.

TABLE I. REPRESENTATIVE RESULTS

(An analytical balance of sensitivity 40 was used, and approximations of the fourth figure were made in the usual manner)

Substance	Sample	H <sub>2</sub> O Found Mg.	CO <sub>2</sub> Found Mg.	H Found %	C Found %	H Calcd. %	C Calcd. %
<i>p</i> -Nitrochlorobenzene	20.70 34.80	4.77 8.10	34.70 58.28	2.56 2.58	45.71 45.66	2.54	45.71
Thiourea	20.30	9.61	11.80	5.26	15.85	5.30	15.78
Benzoic acid	15.84 20.70 34.62	7.04 9.22 15.40	40.04 52.36 87.40	4.94 4.95 4.94	68.94 68.98 68.86	4.92	68.82
Arsanilic acid	22.60 33.85	7.58 11.20	27.54 40.80	3.73 3.68	33.23 33.20	3.71	33.18
2,4-Dinitrophenol	13.40 15.26	2.60 2.96	19.18 21.82	2.16 2.16	39.04 39.00	2.19	39.12
2,4-Dichloroaniline	20.40 22.80 35.64	5.71 6.40 9.90	33.26 37.20 58.10	3.11 3.12 3.09	44.46 44.49 44.46	3.11	44.45
<i>p</i> -Dichlorobenzene	23.42 34.00	5.80 8.50	42.00 61.05	2.76 2.78	48.91 48.97	2.74	48.93
Bromobenzene	18.92	5.52	31.42	3.24	45.29	3.21	45.23
<i>p</i> -Aminobenzoic acid	25.43	11.70	57.00	5.10	61.13	5.11	61.28

With two platinum boats and four absorption tubes, the author has had no difficulty in running as many as sixteen samples in 8 hours (the first sixteen results in Table I). The

number of samples may at first appear large, but as tubes are conditioned by means of a tube conditioner while the second combustion is run, the absorption tubes can be weighed and a new sample made ready for combustion during the sweeping out.

### Summary

A method for filling absorption tubes is discussed whereby combustion time can be materially lessened for semimicro-samples and for microsamples.

The substitution of silver supported on asbestos for silver wool increases the efficiency of the combustion tube in the removal of halogen.

Combustions under increased pressure ensure completeness of oxidation and removal of halogen, sulfur, nitrogen, etc.

Absorptions under pressure ensure complete removal of water and carbon dioxide.

### Acknowledgment

The author is indebted to Mr. Weiskopf of the Technicon Co., New York, N. Y., for his cooperation in the development of this apparatus, and for furnishing combustion tubes of various sizes.

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## A Generator for the Production of Pure Carbon Dioxide

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THE author (2, 3) has described generators which consistently produce carbon dioxide of the high purity required in Pregl's microcombustion method of estimating nitrogen. Modifications of this equipment (1, 4) have corrected some of the imperfections of the original apparatus but, unfortunately, introduced complications and other defects.

A simplified form of the apparatus is represented in the figure. Chambers A and B are conveniently made from 2- and 1-liter Pyrex flasks. The construction of the acid delivery tube, F, ensures a smooth feeding of small drops of solution and eliminates after-drops. The tip should be drawn down to a diameter of approximately 1 mm.

Beginning with the generator completely empty it is charged as follows:

With the generator lying on its side, 170 cc. of concentrated sulfuric acid diluted with 150 cc. of water are introduced into B through E and C, and the acid remaining in C is displaced with air and washed into B with 25 cc. of water. With the generator in the up-

right position, a solution of 500 grams of potassium acid carbonate dissolved in 1100 cc. of water is run into A through D, followed by 100 cc. of water to rinse out the stopcock and bubble trap. The system is evacuated with a vacuum pump through D and E simultaneously for about 15 minutes. Mercury is introduced into the manometer and trap, C, and the generator is set in operation as outlined in a previous publication (3).

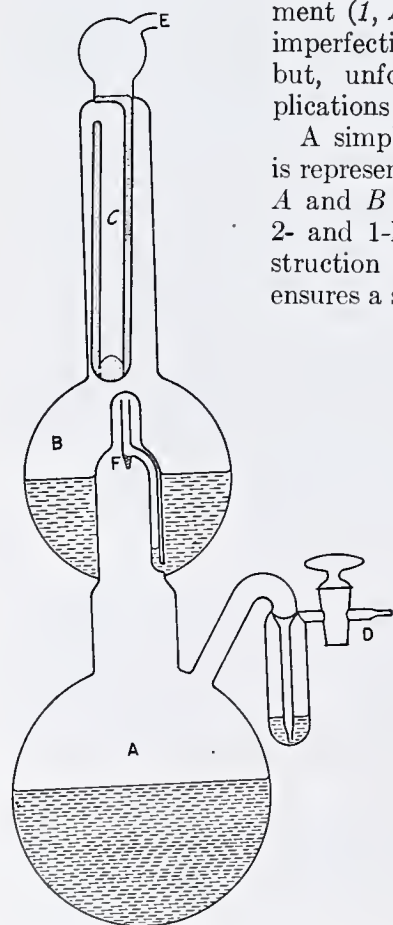
Trap C is constructed with the volume of the inner and outer chambers about equal. Should the pressure in the system, for any reason, fall so low as to break the mercury seal, mercury will be forced into B, and its presence will show that the system has been contaminated with air. In this event the apparatus must be completely emptied and recharged. Any drops of mercury which cannot be removed from bulb B by ordinary means should be dissolved with nitric acid, and the apparatus thoroughly washed to remove nitrates. C is placed in a diagonal position in such a manner that when it is forced the bubbles of gas will travel up one wall. Thus the entire column of mercury cannot be forced into the upper bulb, to prevent action of the trap.

Since the solid potassium sulfate formed in the generator is water-soluble, the generator can be cleaned by running water in at D and out at E. After emptying the generator of water, it is ready for recharging.

This generator will deliver pure carbon dioxide with small fluctuations of pressure, is compact and sturdy, and can be used for the generation of gases other than carbon dioxide. This piece of apparatus is available from E. H. Sargent and Company, Chicago, Ill.

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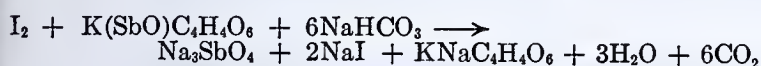
# Tartar Emetic on Leaf and Fruit Surfaces

## Distributional and Semiquantitative Analysis, Using an Iodine-Starch Paper

DONALD STARR, Bureau of Entomology and Plant Quarantine, United States Department of Agriculture, Washington, D. C.

ATTEMPTS to determine the quantity of tartar emetic remaining on citrus foliage during a spraying program led to the realization that in insect control it is sometimes more important to know how the poison is distributed than to know the exact amount present on a given surface. A simple and rapid analytical method was needed if the large number of analyses required in control work were to be handled.

A sensitive iodine-starch test paper was devised which gave a picture of the distribution of the tartar emetic over the leaf surface. The iodometric titration of tartar emetic is a well-known analytical procedure (1) in which the following reaction is involved:



The iodine-starch paper used was dark blue or brown, and the reaction with tartar emetic reduced the iodine and whitened the paper. A semiquantitative estimation of the tartar emetic was made possible by preparing, as a standard of comparison, small slips of paper containing a known quantity of tartar emetic on the surface. The tartar emetic paper

and the citrus leaves were tested with the same iodine-starch paper, and by roughly integrating and comparing the whitened area due to the standard with that due to the unknown the approximate quantities of tartar emetic on the citrus leaves were obtained. The test may also be used for roughly estimating tartar emetic residues on citrus fruit surfaces.

### Preparation of the Test Paper

The iodine-starch mixture used in coating the paper had the following composition: 6.4 grams of iodine, 13 grams of potassium iodide dissolved in a small portion of the water, 54 grams of soluble starch, 3.4 grams of sodium bicarbonate, and 1 liter of water. It is conveniently prepared by adding the starch and sodium bicarbonate to 1 liter of a stock solution of 0.05 *N* iodine. The effect of varying the proportions has not been studied extensively, but the above amounts may be altered without markedly affecting the results. Larger quantities of sodium bicarbonate increased the fading of the paper; however, when sodium bicarbonate was absent the sensitivity was decreased. The amount of water used depends upon the sensitivity of the reaction desired. The more concentrated mixtures give darker and better coats of iodine, but the reaction is less sensitive.

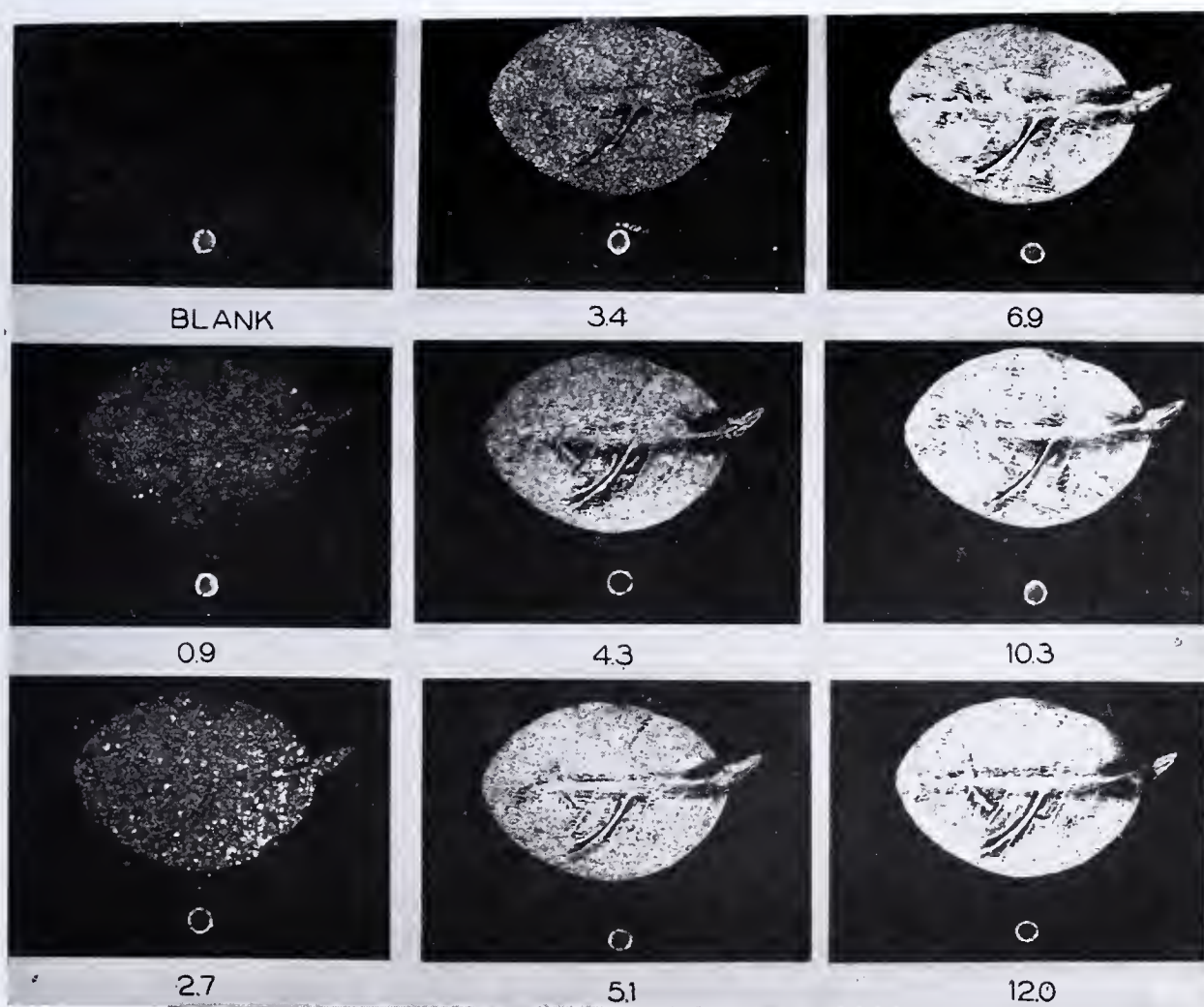


FIGURE 1. PRINTS OF TARTAR EMETIC ON GRAPEFRUIT LEAVES USING THE MORE SENSITIVE TEST PAPER. Numbers indicate tartar emetic concentration in micrograms per square centimeter. Each circle represents 10 micrograms.



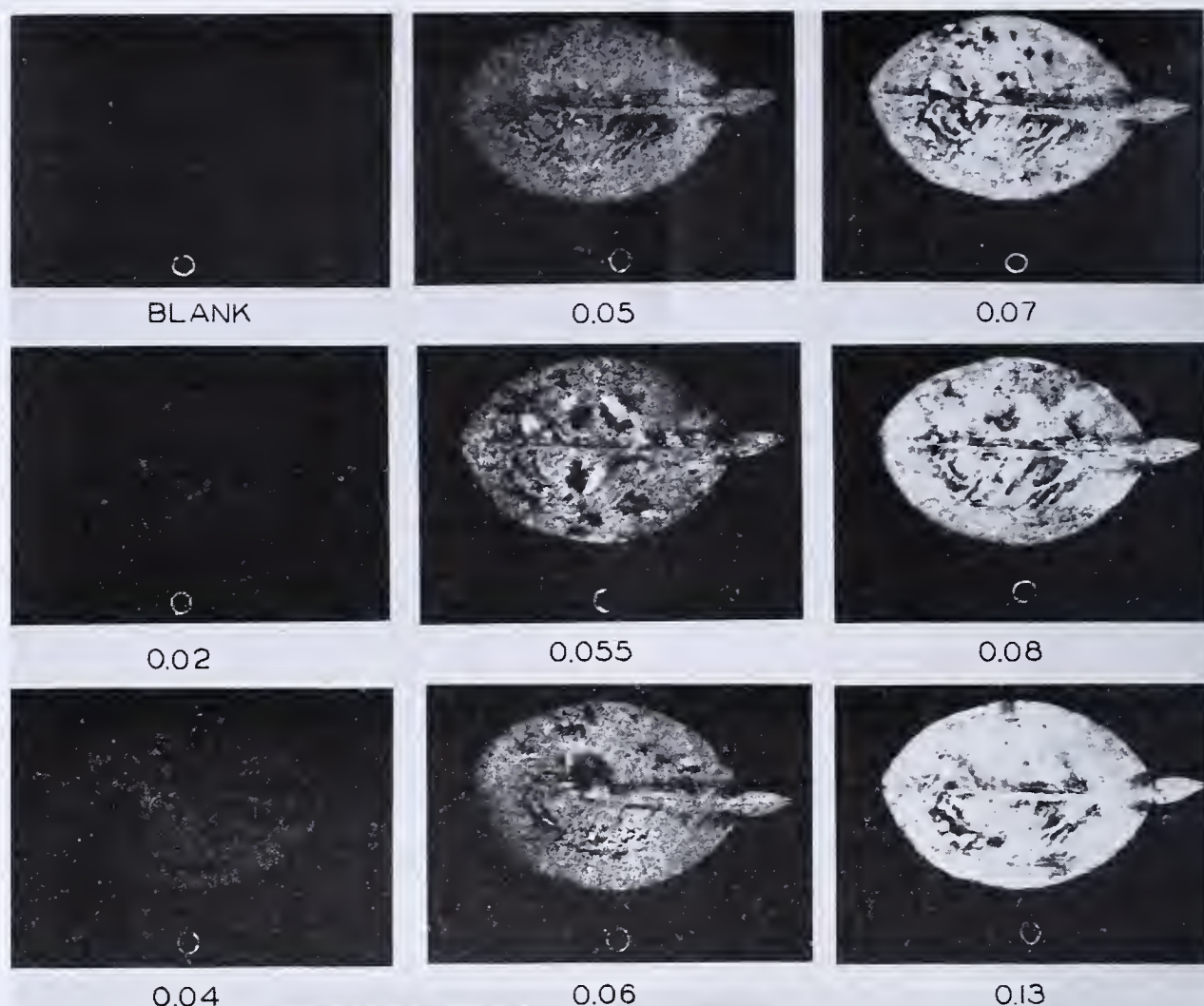


FIGURE 2. PRINTS OF TARTAR EMETIC ON GRAPEFRUIT LEAVES USING THE PAPER WITH THE HEAVIER COATING OF IODINE

Numbers indicate tartar emetic concentration in milligrams per square centimeter. Each circle represents 0.02 mg.

The paper which gave the best results in these studies was manifold typewriting paper of about 9 pounds per ream, 17 by 22 inches, containing 500 sheets. The methylene blue size test (as used at the Institute of Paper Chemistry) was about 30 seconds. Some heavier, harder sized sheets took a thinner and less uniform coat. A lighter paper took a fair coat, but the uniformity and opacity were poor. Filter paper did not take a uniform coat.

The paper was dipped into the iodine-starch mixture until thoroughly wet, and then removed, drawn over a 12-mm. glass rod to remove the excess, and hung up to dry.

The iodine-starch mixture may be used or stored for 3 or 4 weeks, but the coat obtained gradually becomes lighter in color. The paper fades noticeably after it has been kept for 1 or 2 months. Increasing the sodium bicarbonate content and exposure to sunlight accelerates fading. Iodine-starch paper kept in a small air-tight container away from the light had faded slightly after a month, but it was in better condition than when kept in the open, exposed to air and light.

In general, the strength of the coating mixture should be varied to suit individual needs, depending on the time the paper is to be stored before use, on the sensitivity of the reaction desired, and on the way the paper takes up the iodine-starch mixture.

### Preparation of the Standard Tartar Emetic Paper

Different amounts of tartar emetic were used to prepare the standard paper, but 0.01 or 0.02 mg. was found to be satisfactory.

The standard papers were prepared using a microburet which delivered a drop of distilled water having a volume of 0.045 cc. at 22° C. at a speed of 1 drop in 3 to 5 seconds. Using 0.00133 *N* tartar emetic solution to prepare 10-microgram standards and 0.00266 *N* for the 20-microgram standards, 80 drops represented 3.595 cc. in the first case and 3.615 cc. in the second. The average differences are 0.14 and 0.42 per cent from the volume on which the calculations were based.

The paper was such that the solution would stand up well and upon drying leave a ring of tartar emetic 5 to 7 mm. in diameter.

Alcohol was added to the solution in attempts to produce a spot of tartar emetic rather than a ring. Up to 50 per cent by volume of alcohol, with 20 micrograms contained in a drop of 0.02 cc. of the solution when applied to the paper still gave a ring, but 10 to 14 mm. in diameter.

Sodium thiosulfate standards equivalent to 10 micrograms of tartar emetic also gave ringed deposits.

### Recommended Testing Procedure

The degree of reaction obtained between the iodine-starch test paper and the tartar emetic standard paper increases with time, temperature, and pressure. A nearly complete reaction is obtained in 15 minutes at 20° to 25° C. with a pressure of 100 to 150 grams per square centimeter, but qualitative tests on grapefruit leaves and fruit have been very distinct in a minute or less. It has been determined experimentally that the reaction from grapefruit leaves, dorsal surface, and from glass surfaces is faster than from the standard paper. If the pressure used is less than 100 grams per square centimeter, it may be necessary to increase the time in order to get a complete reaction.

The test is run by placing the standard paper beside the leaf and pressing the test paper against them with a well-moistened pad made of about eight thicknesses of filter paper backed by about eight thicknesses of muslin toweling and four thicknesses of turkish toweling. (In the laboratory a weight of about 20 kg. was applied to thick glass plates of 160-sq. cm. area, but in the field A. C. Baker found it convenient to use a small photographic printing frame.) The



leaf can be tested on both top and bottom surfaces by placing it between two test papers with moist pads above and below.

If permanent records of the tests are desired, brown or blue prints may be made from the iodine-starch test paper. The prints must be exposed accurately to bring out the tartar emetic spots without smudging the paper. Iodine-starch prints fade considerably after one or two months.

The sensitivity of the test has been increased by diluting the coating mixture. A paper prepared as described above gave a distinct reaction with 0.0005 cc. of a solution containing 2.0 grams of tartar emetic per liter, or 1.0 microgram of tartar emetic. A more sensitive paper prepared from the above formula with the sodium bicarbonate doubled, and diluted with seven parts of water reacted to 0.1 microgram of tartar emetic.

Figures 1 and 2 are photographs of prints taken from grapefruit leaves dusted with varying known amounts of tartar emetic. It will be noted from Figure 1 that the tartar emetic concentration can be tested within the range of 0.9 to 10 micrograms per square centimeter using the more sensitive paper mentioned above. With the higher concentrations—namely, 0.02 to 0.13 mg. per square centimeter—paper prepared from the undiluted mixture may be used. The results are shown in Figure 2. The photographs indicate the degree of precision obtainable under the prescribed conditions.

The distribution of tartar emetic on citrus leaves after being

sprayed with tartar emetic solutions is much less uniform than that obtained by dusting.

### Interfering Substances

The materials that may be expected to interfere with the test are reducing substances in general. Some of the materials found to interfere are sodium arsenite, glue, and molasses. The paper is not very sensitive to arsenious oxide or Paris green, probably owing to the low solubility of these compounds. Sucrose, glucose, fructose, galactose, arabinose, and xylose were found to be nonreactive, or so nearly so that there would be no interference. Strong ammonia solution, calcium hydroxide, and potassium carbonate reacted with the paper. Strong alkalies in general react with iodine to give hypoiodites.

### Summary

Iodine-starch test papers have been prepared for the purpose of obtaining distributional and semiquantitative analyses of leaf surfaces for tartar emetic. The test is sensitive to 0.9 microgram per square centimeter.

Known quantities of tartar emetic have been deposited on paper as a standard of comparison.

Substances that reduce iodine interfere with the test for tartar emetic.

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## Ejector-Type Evacuator for Wet Assay Systems

EDGAR J. POTH, Stanford University School of Medicine, San Francisco, Calif.

THE elimination of corrosive fumes evolved in wet assay methods such as Kjeldahl digestions frequently presents a problem, especially in poorly planned laboratories. One is faced with the problem of disposing of corrosive fumes as well as removing them from a given system. For the elimination of fumes created in many microanalytical procedures, a small digestion chest is presented (Figure 1, G). It is made of stainless steel, has a removable top, and, after use, can be washed out thoroughly. It can be placed on a hot plate.

The ejector or jet pump is constructed of Pyrex glass and operates with high efficiency on low-pressure steam. The fumes are brought into direct contact with live steam, which in turn is condensed by a spray of cold water. In this way the corrosive materials either react with the steam or are dissolved in the condenser water. Furthermore, they are highly diluted and can be dumped directly into the ordinary laboratory drainage system. The pump will handle liquids as readily as vapors and so it is not necessary to have traps for liquids condensing in or introduced into the system.

In the construction of this pump it is well to determine experimentally the position where any particular jet gives the greatest efficiency with the steam pressure available.

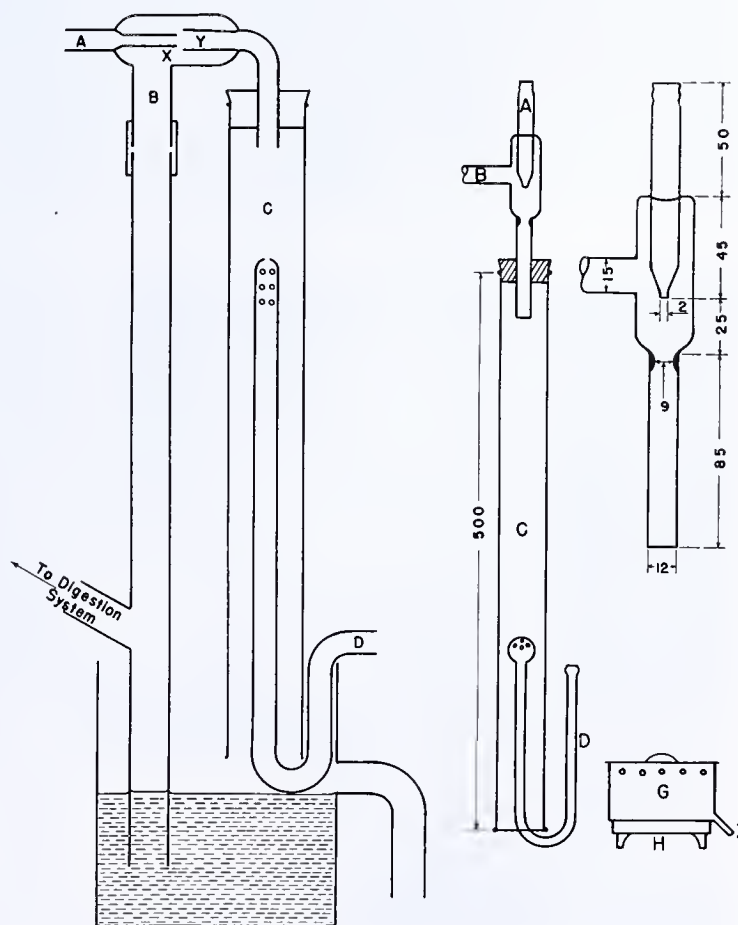


FIGURE 1. EJECTOR-TYPE EVACUATION PUMP

(See designations at left)

- A. Steam inlet and jet
- B. Vacuum outlet to connect with digestion system
- C. Condenser
- D. Spray condenser
- G. Digestion box made of stainless steel
- H. Hot plate
- I. Fume and spillway to be connected with B

- X. Male half of steam jet, 5 mm. in inside diameter
- Y. Female half of steam jet, 12 mm. in inside diameter, slightly tapered. Gap between X and Y measures 4 mm.

Dimensions in millimeters. Design on right best suited for system of small capacity; design on left, illustrated with sump and overflow water trap, best for systems of large capacity.



# MODERN

# LABORATORIES



## Modernization of Norwich Laboratories

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THE new laboratories of the Norwich Pharmacal Co., which were opened in March of this year and are the finishing touch to a complete plant-modernization program, are not only a marked improvement over the former laboratories of this company but present many features and innovations new to laboratory construction. The space now occupied by the laboratories was formerly the pill-coating department and is located on the third floor of a conventional brick factory building having an interior of exposed wooden beams and flooring and a double row of supporting pillars about 15 feet apart and 17 feet from the brick side walls. Yet in this typical factory setting there has evolved a modern, clean, well lighted laboratory.

The first step in the modernization was to cover the side walls and supporting pillars with green marlite, a synthetic plastic board with a high reflective surface. The ceiling has been made flush by covering the beams with a cream-colored marlite. A modern ring reflector lighting system has been installed and sprinkling jets have been brought out at necessary places. The use of this synthetic plastic board gives a

hard, fume-resisting surface which is easy to clean and because of its light-reflective properties makes the laboratory much brighter than those laboratories using the usual white flat paint.

The supporting columns have been made a part of the laboratory bench by designing equipment to fit around them. Individual bays have been made on both sides of the room, a portion of the space between columns serving as a center main aisle. The bays are U-shaped and contain a center work bench built about a column, two side work benches also built about columns, and two steel desks along the wall, or bottom portion of the U. Here the similarity to most laboratories ends and the novel features of this new laboratory start. Each bay has been separated from the next by plate glass which extends from the top of the side laboratory benches to within a few inches of the ceiling. Such plate-glass dividers increase the amount of light received in the bay, give an effect of spaciousness, and allow privacy for conversation without completely shutting off each unit; yet each worker has the necessary isolation for efficient work. By not

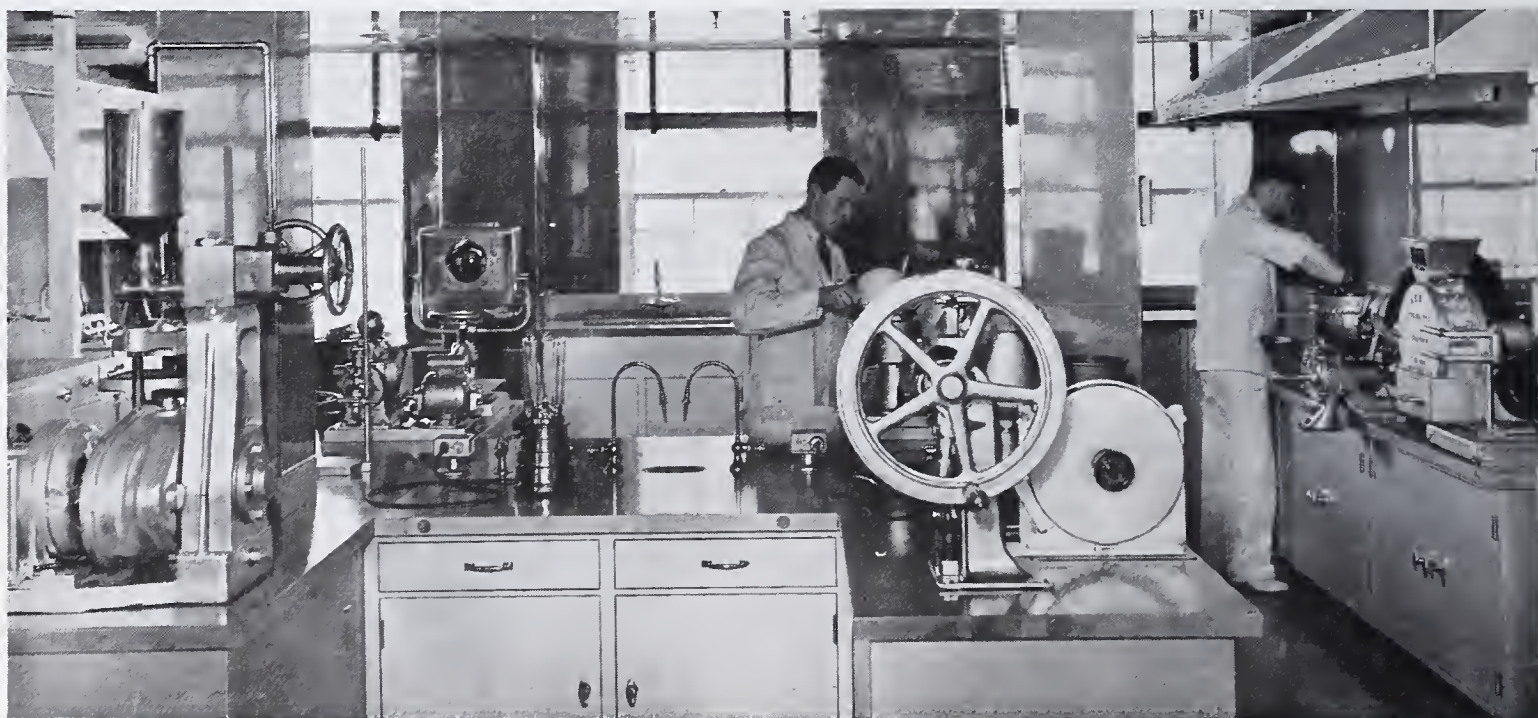


FIGURE 1. PILOT PLANT AFTER MODERNIZATION



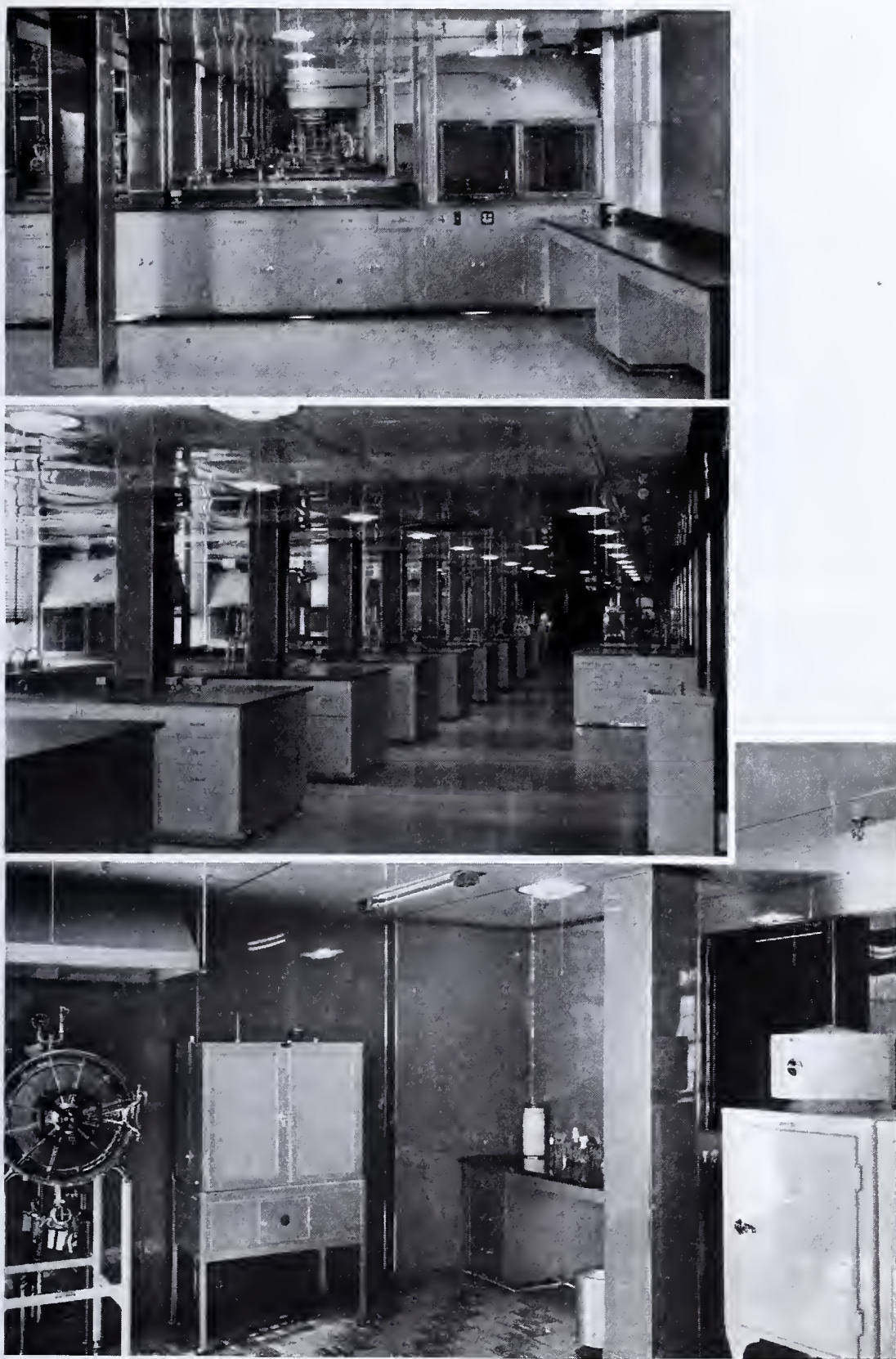


FIGURE 2. MODERNIZED LABORATORIES

*Top.* Looking towards front through plate-glass partitions, steel desk at right. *Center.* General laboratory, plate-glass dividers at left center, individual fume hoods, no reagent shelves. *Bottom.* Bacteriological laboratory. Long tube on ceiling is sterilizing lamp.

extending the plate glass to the ceiling one air-conditioning outlet may serve a number of work spaces.

Peg boards, glassware cabinets, etc., have been eliminated and all glass apparatus has its proper storage space in the specially designed steel benches. There are no drainboards or storage spaces on top of the work bench for dirty glassware. Each chemist stores his dirty utensils in a specially designed stainless steel tray which fits into one of the end drawers of the work bench. The drawer has been constructed so that

the face may be swung downward and the tray slipped out. All dirty apparatus is collected at intervals and transported to a washing room. When clean, the apparatus is returned to the bench from which it came.

Reagent shelves, chemical storage shelves, etc., have also been eliminated. Reagents have been placed in specially designed wooden trays which are also stored in a bottom drawer of the work bench. For routine analytical procedures, reagents for each type of analysis are stored in separate





FIGURE 3. LABORATORIES BEFORE MODERNIZATION  
 Pilot plant in center, bacteriological laboratory at bottom

trays and at the beginning of each work day, or at the beginning of each analysis, the proper tray is lifted out and put on the work space. As each analysis is completed the tray containing the reagents is put back into its proper space.

The equipment was designed for each type of individual project. Although storage drawers and closets are conventional there are several unique features, such as waste receptacles which have been designed to fit underneath the sinks. Slits have been cut in the bench door in front of the receptacle and a small chute or neck leads to the waste pan, assuring proper disposal. Another feature is the constant-temperature closet housing the shaking mechanism which has been installed in the bottom end of the bench devoted to routine analytical procedures.

Frogs used in biological tests have a specially designed storage tray in the pilot plant section of the laboratory. Temperatures in this tray are kept close to freezing in order to maintain these animals in their dormant state. Adjacent to the animal tray are two special units, one refrigerated in which preparations for sale in the colder sections of the world are tested, and one electrically heated for testing products shipped to tropical regions.

The pilot plant is equipped with laboratory-size production equipment such as filter presses, pill-coating machines, dryers, ball mills, fractionating apparatus, kettles, etc., and can duplicate any unit process used in manufacturing operations.

Each chemist has a fume hood adjacent to his desk. Each fume hood has a permanent, recessed, stainless steel water bath with an alberene stone top, and service facilities for hot and cold water, air, vacuum, gas, and steam. Each hood has an individual exhaust fan and an outside control for the gas line. The bottom portion of the rear partition and the top or exhaust part of the fume hoods are adjustable, thereby allowing a regulation of the draft space. For heavy gases the rear aperture could be made smaller, ensuring an increased velocity of incoming air.

All benches, desks, and cabinets are of aluminum-painted steel. Cabinets have adjustable shelves and each stone table top has several small cone-shaped drains lined with stainless steel for use on condenser water lines, and two small steam baths served with low-pressure live steam. These baths are used to warm flasks of inflammable chemicals and solvents, thereby making unnecessary the use of oil and sand baths except where high temperatures are needed.

A titration service area is located against the side wall of the bay devoted to routine analysis and with one exception partitions and superstructures have been eliminated. This exception is the bacteriological laboratory, which had to be separated from the main area, as the air is carefully filtered and sterilized. A sterilizing lamp can be seen in the picture of the bacteriological laboratory.

As a matter of convenience the center main aisle serves to separate the two activities of the laboratory, one side being devoted to control and analysis of raw and finished materials, the other to research, pilot plant, and bacteriological work.

Expensive and infrequently used apparatus has been placed on the center aisle end of the benches. In this manner equipment may be used without disturbing other workers and without requiring a special instrument room. A library and reading room are located at the end of the laboratory area.

A central main washing room and a chemical storage space serve the chemical as well as the company's animal laboratories.

### Acknowledgment

The assistance of Francis Chilson, consulting engineer, in the modernization of the Norwich plant is gratefully acknowledged.



# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION

Harrison E. Howe, Editor

## Determination of High Viscosities

By Means of the Gardner Mobilometer

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A setup for Gardner mobilometers is described, whereby accurate temperature control and easy operation are obtained. The conclusions of Cornthwaite and Scofield that the correlation between absolute viscosity and mobility is a straight line have been checked by the authors for much higher vis-

cosities, at various temperatures, and for different disks. Provided rigid control of time and temperature is obtained and improvements in mechanical construction are made, the mobilometer can be used as a precision instrument for the determination of absolute viscosity.

THE mobilometer, originally described by Gardner and Parks (3), was designed to be used as a production control instrument to secure uniformity in consistency between different batches of a given product. The instrument was first recommended for control in paint and lacquer manufacturing. Later, Gardner and Van Hueckeroth (4) extended its use to the testing of food products, mineral oils, vaseline, and coal tar. The instrument has also been described at length by Sward and Stewart (6). While no claim for high accuracy of results obtained with the instrument was made by Gardner and Parks (3), Cornthwaite and Scofield (2) showed that under rigid control of temperature and time the apparatus gave a remarkably close correlation with the absolute viscosity of a number of samples possessing true fluid flow. This correlation resulted in a straight line passing through the origin when plotted on rectangular coordinates.

The work of Cornthwaite and Scofield (2) was, however, limited to oils of relatively low viscosities (about 8 poises). It was necessary for this laboratory to determine a number of mobilities and viscosities of much higher values with a fair degree of accuracy. For this purpose the relationship between viscosity and mobility for true fluids was obtained at various temperatures, using oils of much higher viscosities. The apparatus is described below.

### Apparatus

In order to obtain flexibility and, at the same time, accurate temperature control, the barrel of the mobilometer was provided with a brazed outer brass jacket about 0.5 inch wide fitted with outlets at the top and bottom. These outlets are connected by means of rubber tubing to the circulation outlets of a Hoeppler (5) thermostat which is capable of controlling the temperature to within  $\pm 0.02^\circ \text{F}$ . This apparatus provides a very flexible control of the temperature and, by using the proper circulation fluid and regulator in the Hoeppler thermostat, it is also suitable for low-temperature work, as shown by the authors in a previous article (1). The necessity of immersing the whole mobilometer in a bath is thereby avoided, which is an important advantage when working at extreme temperatures.

Timing in this laboratory is obtained by Veeder-Root magnetic counters, reading directly in tenth seconds. These are run by a contactor connected to an American Time Products constant-frequency generator. This generator, which is run by the plant power, allows a fluctuation of  $\pm 10$  volts and a frequency variation of  $\pm 2$  cycles in the current. Under these conditions the frequency does not vary by more than  $\pm 0.001$  cycle. This arrangement has given complete satisfaction, the frequency fluctuations having seldom exceeded the above limits. A more complete description of this equipment will be published in the near future. Viscosities were carried out by means of Ubbelohde (7) suspended level viscometers. A No. 4 capillary (constant  $C = 10.04$ ) was generally used, except for the lower viscosities which were obtained with a No. 3 capillary (constant  $C = 1.015$ ). The results thus obtained were in kinematic units. The absolute viscosities were calculated by multiplying the kinematic results by the density (obtained by pycnometer) of the individual samples at the various temperatures. The above procedure will give kinematic viscosities within  $\pm 0.2$  per cent while the densities were accurate to about 0.001. The constant-temperature bath used for the determination of kinematic viscosities can be controlled to within  $\pm 0.02^\circ \text{F}$ .

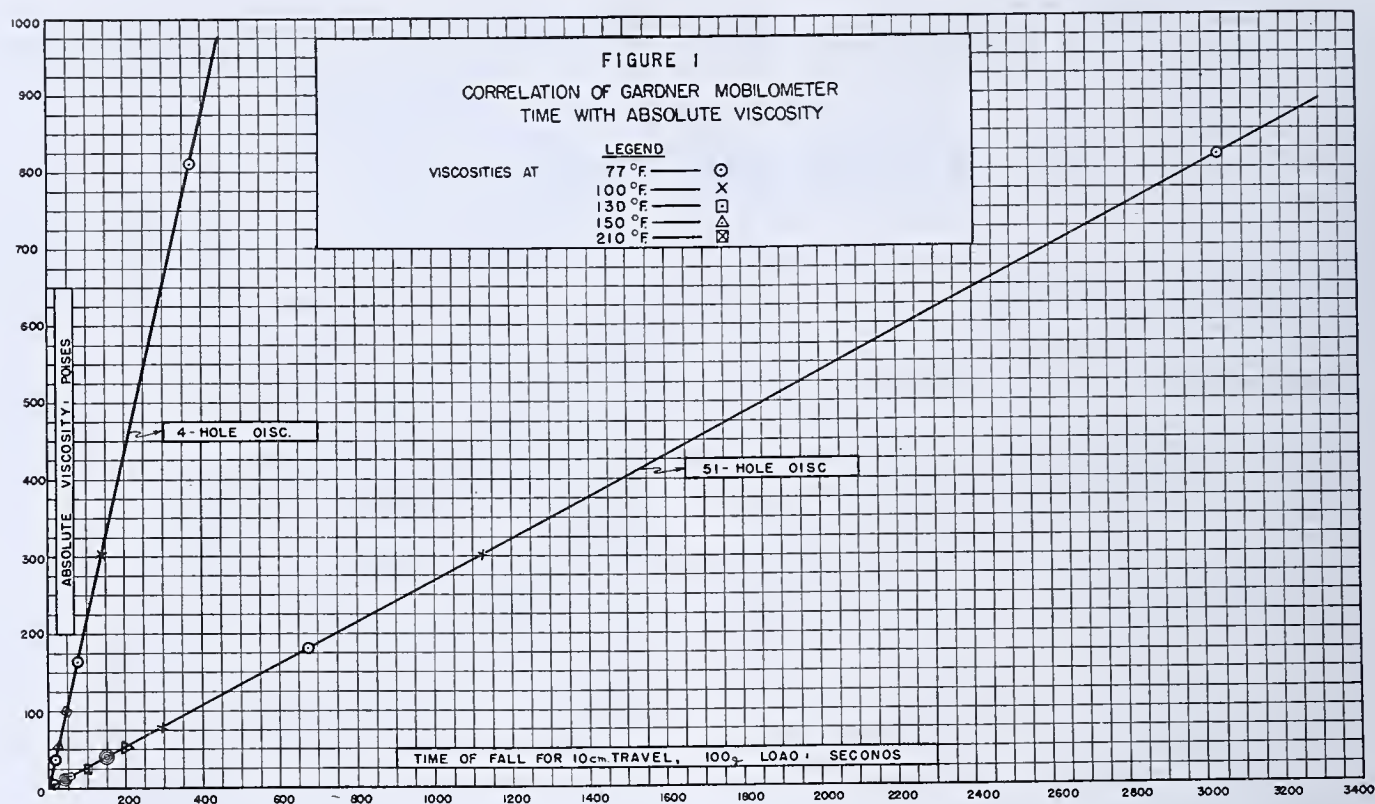
### Results

The choice of materials available for the determination of viscosities by means of viscometers of the glass capillary type is limited by the following considerations:

1. The material must have true viscous flow—i. e., the rate of shear should be proportional to the shearing stress.
2. It must be a true solution, absolutely free of suspended particles.
3. It must be transparent, so that a sharp meniscus can be seen when determining the viscosity.

The heaviest Pennsylvania bright stock available had a viscosity of about 163 poises at  $77^\circ \text{F}$ . In order to obtain high viscosities, especially at the higher temperatures, it was necessary to prepare blends of the above mineral oil with various amounts of an isobutylene polymer of very high molecular weight. Thus viscosities as high as 800 poises at  $77^\circ \text{F}$ . and 300 poises at  $150^\circ \text{F}$ . were obtained. Determina-





tions of both viscosities and mobilities were carried out at 77°, 100°, 130°, 150°, and 210° F. Mobilities were also carried out with both a 51-hole and a 4-hole disk. The results are shown in Figure 1, which is self-explanatory. (Concentric rings indicate determinations made on different materials having the same viscosities.)

### Conclusions

From an examination of the curves shown in Figure 1, the following conclusions can be drawn:

The correlation between Gardner mobilometer time (in seconds) and absolute viscosity (in poises) is a straight line passing through the origin.

The above statement holds true for determinations made at various temperatures, and for different disks, although, as should be expected, changing the disk changes the slope of the curves. In other words, each disk has its own curve passing through the origin.

The results check the work and conclusions of Cornthwaite and Scofield (2) in every respect. However, the slope of the curve obtained by these authors for their 51-hole disk is not quite the same as that presented in this paper. This is due to the fact that it is mechanically impossible to manufacture disks identical in all respects; small variations in the shape of the disk as well as in the sizes and spacing of the holes will

cause changes in mobilities and thus alter the slope of the curve.

While admittedly the mobilometer is primarily a control instrument, it is susceptible of mechanical improvement. It is based on sound principles and the data presented show that it can be used for the determination of viscosity, being particularly useful for opaque materials of very high viscosities. It is only necessary to calibrate each disk against a material of known viscosity at any given temperature, plot this point, and draw a straight line through the origin. The sizes and number of holes in a given disk can be varied at will to suit any particular case.

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# Phenols in Low-Temperature Tar

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VARIOUS workers have identified individual dihydric phenols in the products of the low-temperature carbonization of bituminous coals, including resorcinol (13, 14), hydroquinone (13, 14), catechol (1, 2, 3, 5, 9, 11-17), and some of the homologs of catechol (4, 13, 14), but ratios of the dihydric to the monohydric phenols produced during carbonization have not been reported. This paper describes a method by which this ratio, or, more specifically, the average number of hydroxyl groups per molecule of the phenols of a tar, may be determined, and gives the results obtained by applying it to the tars produced by carbonizing several bituminous coals at temperatures from 400° to 600° C.

The usual method of analysis, which involves the double distillation of the tar and alkali extraction of the distillate in the presence of air, is not satisfactory for the determination of the quantity of dihydric phenols present in a tar, because of the instability of these phenols toward heat and oxidation, particularly in the presence of alkali. The double distillation causes sufficient decomposition of these phenols to preclude the possibility of an accurate quantitative determination of their presence in the tar as originally produced. The alkali extraction of the tar distillate in the presence of air continues the decomposition to such an extent that by the time the phenols have been separated from the other constituents of the tar, only a small portion of the dihydric phenols may be left. In the present method, the tar is not distilled. The quantity and type of the phenols as they exist in the whole tar, rather than in the tar distillate, are determined.

Briefly, the method consists of extracting a tar with alkali in an inert atmosphere to prevent oxidation, methylating the alkali phenolates to stabilize the hydroxyl groups, and recovering the methylated phenols. From the methoxyl percentage and average molecular weight of these latter, their average number of methoxyl groups per molecule is calculated. This value also represents the average number of hydroxyl groups per molecule of the phenols originally in the tar. From it the ratio of dihydric to monohydric phenols may be calculated, provided it be assumed that dihydric phenols are the only polyhydric ones present.

Carrying out the alkali extraction of the tar, and the subsequent methylation, in an atmosphere of nitrogen was effective in preventing oxidation of the tar. When a 500° tar from a Pittsburgh Seam coal was extracted with alkali in the presence of air, an appreciable quantity of a solid decomposition product was precipitated out on the sides of the separatory funnel. When a similar extraction was carried out in an atmosphere of nitrogen, this evidence of decomposition was absent. The alkali extraction offers another difficulty, however, in that the alkaline solution dissolves not only phenols but neutral material as well, because of the solubility of hydrocarbons in the solution of alkali phenolates. This difficulty was overcome by extracting the alkali phenolate solution with benzene, again carrying out the extraction in an atmosphere of nitrogen. The benzene, however, removed not only the hydrocarbons, but also a small quantity of the phenols. These phenols were recovered by extracting the benzene solution with fresh alkali. There was slight tendency for the hydrocarbons to redissolve in the alkali, as their solubility in the alkaline solution depends upon the presence of appreciable quantities of alkali phenolates.

The methylation was effected by means of dimethyl sulfate, which apparently gave a complete reaction when used in

excess. The excess was destroyed with alkali, which also hydrolyzed any esters that may have been formed from the carboxylic acids in the alkali phenolate solution. The methylated tar phenols are much more stable than the corresponding phenols. They are not so unstable toward heat as the phenols, and show little tendency toward oxidation when standing in air. This last property made it possible to discontinue the use of an inert atmosphere as soon as the methylation was completed, and permitted the methoxyl percentage and the average molecular weight of the methylated phenols to be determined with little danger of decomposition during the necessary handling.

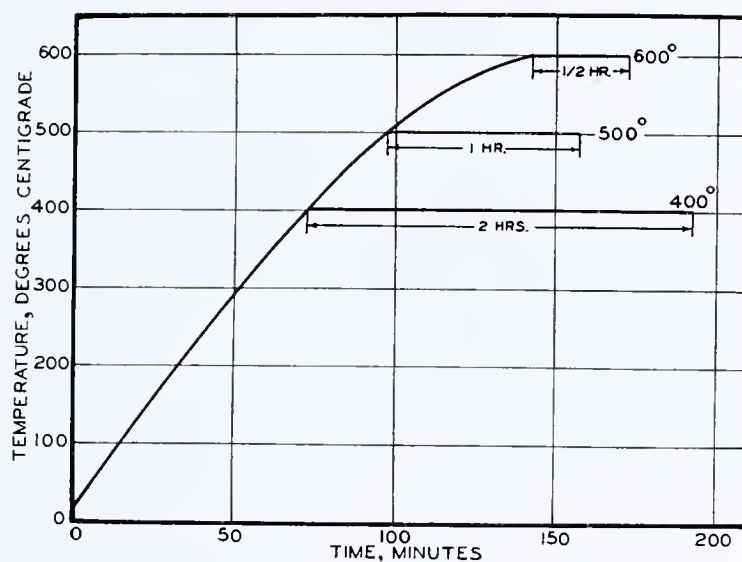


FIGURE 1. TEMPERATURE PROGRAMS FOR CARBONIZATIONS IN THE FISCHER ALUMINUM RETORT

The entire method was applied to a mixture made up of 2,6-xylenol, tetralin, *p*-cymene, *n*-heptane, cyclohexanol, biphenyl, *o*-toluidine, and acetic acid. The methylated xylenol was obtained in a pure form with a yield of better than 93 per cent of theory. The methylation step alone was checked by methylating catechol. The veratrole resulting amounted to 97 per cent of theory.

## Experimental

The tars analyzed in this study were produced in a Fischer aluminum retort (10). Each charge consisted of 100 grams of the coal, ground to 20- to 60-mesh size. The retort was subjected to the temperature programs shown by the curves of Figure 1. For each carbonization the sample was heated rapidly to the desired temperature and maintained at this temperature until there was no visible evidence of distillation of tar from the exit tube of the retort. Throughout the heating, nitrogen was passed into the retort at a rate of 20 cc. per minute. The tar and liquor were collected in a small side-arm separatory funnel immersed in crushed ice. As soon as a carbonization was completed, the receiver was stoppered and weighed to determine the amount of tar plus liquor formed. A source of nitrogen was then connected to the side arm of the receiver, and the tar and liquor were extracted successively with 15-, 10-, and 10-cc. portions of 5.5 *N* potassium hydroxide. The solution of phenolates was extracted with three 20-cc. portions of benzene, which was then extracted with two 10-cc. portions of 5.5 *N* potassium hydroxide. All the extractions were carried out in an atmosphere of nitrogen. The alkaline solutions were combined, and enough 15 *N* potassium hydroxide was added to make the solution 6 *N*, allowing for the diluting effect of the liquor that was formed with the tar.



TABLE I. ANALYSES OF COALS USED

Seam	Mine	Bituminous Rank	Proximate Analysis <sup>a</sup>			Moisture in Sample Carbonized %	Ultimate Analysis <sup>b</sup>				
			Volatile matter %	Fixed carbon %	Ash %		C %	H %	N %	S %	O %
Pittsburgh	Edenborn	High-volatile A	33.6	57.0	7.5	1.4	85.0	5.7	1.7	0.7 <sup>c</sup>	6.9
Illinois No. 6	Orient No. 1	High-volatile B	33.9	50.3	9.1	8.2	80.6	6.1	2.1	0.7 <sup>c</sup>	10.5
High Splint	Clo-Splint	High-volatile A	36.4	57.3	3.4	3.9	83.8	5.7	1.8	0.6 <sup>d</sup>	8.1

<sup>a</sup> Analyses of mine and tippie samples, courtesy of U. S. Bureau of Mines, Pittsburgh Experiment Station.

<sup>b</sup> Dry, mineral-matter-free basis (mineral matter = 1.1 times ash).

<sup>c</sup> Organic sulfur only.

<sup>d</sup> Total sulfur.

TABLE II. ANALYSES OF TARS PRODUCED IN FISCHER RETORT

Carbonizing temperature, ° C.	High Splint Coal			Edenborn Coal			Illinois No. 6 Coal					
	400	500		400	500		600	400		500		600
Tar yield, grams <sup>a</sup>	8.3	16.5	16.2	5.0	14.2	13.8	14.5	6.2	6.4	13.4	13.5	12.9
Liquor yield, grams <sup>a</sup>	5.6	6.2	6.1	2.3	3.9	3.8	3.7	11.0	11.4	11.2	11.2	13.2
Methylated phenols, yield, grams <sup>a</sup>	2.0	4.7	4.7	0.6	3.7	3.4	3.6	2.6	2.9	5.0	5.1	5.4
Methylated phenols, % MeO	17.50	17.86	17.96	18.53	16.89	16.86	16.72	22.23	21.84	19.10	18.98	20.76
Methylated phenols, molecular weight	192	181	181	207	206	207	202	173	174	165	168	154
Average hydroxyls per phenol molecule	1.084	1.043	1.049	1.237	1.123	1.127	1.091	1.241	1.227	1.017	1.029	1.031
Dihydroxy compounds in phenols, %	8.4	4.3	4.9	23.7	12.3	12.7	9.1	24.1	22.7	1.7	2.9	3.1
Phenols, yield, grams <sup>a</sup>	1.8	4.3	4.3	0.55	3.4	3.1	3.3	2.3	2.6	4.6	4.7	4.9
Phenols, yield, % of tar	21.7	26.0	26.5	11.0	24.0	22.4	22.8	37.1	40.6	34.3	34.8	38.0
Phenolic oxygen, grams <sup>a</sup>	0.182	0.433	0.435	0.057	0.322	0.296	0.311	0.298	0.326	0.494	0.500	0.579
Organic oxygen in 100 grams of coal, grams		7.50			6.34					8.68		
Phenolic oxygen, % of organic oxygen	2.4	5.8	5.8	0.9	5.1	4.7	4.9	3.4	3.8	5.7	5.8	6.7

<sup>a</sup> From 100 grams of coal.

The benzene extraction of the phenolate solution was necessary because of the high solubility of hydrocarbons in the phenolate solution. In one case the weight of neutral material dissolved by the alkali was 40 per cent of the weight of the phenols dissolved. The quantity of phenols redissolved by the benzene was small, but these phenols were lower in molecular weight than those remaining in the alkaline solution, so that it was necessary to recover them in order to get a true picture of the average composition of all the phenols.

Methylation was carried out by adding the alkali phenolate solution slowly to a stirred mixture of dimethyl sulfate and benzene held at about 70° C. The quantity of dimethyl sulfate used was about 50 per cent in excess of that required to convert all the alkali to potassium methyl sulfate. Initial heating only was necessary, as the reaction was exothermic. Once the reaction was started, the temperature could be regulated by means of the rate of addition of alkali phenolate solution. After this solution had been completely added, twice the amount of 15 *N* potassium hydroxide equivalent to the remaining dimethyl sulfate was added to the hot methylating mixture. After the destruction of the excess dimethyl sulfate, two layers remained. The aqueous layer contained the salts of the carboxylic acids originally in the tar, and the benzene layer the methylated phenols. This layer was washed several times with alkali and water, and dried, and the benzene was removed by distillation followed by evacuation.

The methoxyl percentage of the methylated phenols was determined by a modified Vieböck micromethod. Analyses for sulfur were made to ascertain whether the dimethyl sulfate, which would raise the methoxyl percentage, had been completely removed from the methylated phenols. Their average molecular weight was determined cryoscopically using biphenyl as a solvent. Apparent molecular weights were determined for several different concentrations, and the value obtained by extrapolating to zero concentration taken as the true average molecular weight. The molecular weights of several pure aromatic ethers were determined by this method with errors of less than 2 per cent, and checks within 4 per cent were obtained on the methylated phenols from the tars.

Analyses of the coals used are shown in Table I. The Pittsburgh Seam coal is a high-volatile A coking coal, the Illinois No. 6 coal is high-volatile B and has a high oxygen content, which barely falls within the limits for coking coals. The High Splint coal is likewise high-volatile, but in contrast to the other two is dull and contains a high percentage of attritus.

Table II gives the results of the analyses of the tars produced under the indicated conditions from the various coals. Yields of tar and liquor were determined in separate carbonizations, as no separation of tar from liquor was made during the analyses. The average numbers of hydroxyl groups per phenol molecule were calculated from the methoxyl percentages and average molecular weights of the methylated

phenols, shown just above in Table II. The percentages of the phenols which are dihydric, assuming that there are no trihydric or higher phenols present, follow directly. This assumption is based on the facts that the probability of forming trihydric phenols is much lower than that of forming dihydric phenols, and that the presence of trihydric phenols in tar has never been reported. The yields of phenols, as calculated from the experimentally determined yields of methylated phenols, and the phenolic oxygen, as per cent of the organic oxygen in the coal, are also shown in Table II.

### Discussion of Results

The high ratios of dihydric to monohydric phenols in the tars made from Edenborn coal are the most striking feature of the results. The ratio decreased as the temperature of carbonization was raised (see Figure 2). This change may be accounted for if the known instability toward heat of the dihydric phenols is considered. The tendency to produce oxygenated compounds high in polyhydric phenols appears to be characteristic of this Pittsburgh Seam coal. This tendency, however, cannot be linked to the classification of the coal, on the basis of the present data. The High Splint coal, which differs from Edenborn coal mainly in that it is a dull instead of a bright coal, gave less than half the yield of dihydric phenols that was obtained from Edenborn coal.

The Illinois No. 6 coal, because it has a higher oxygen content, might be expected to produce phenols having a larger average number of hydroxyl groups per molecule than those from Edenborn coal. The increased oxygen content might increase the probability of two oxygen atoms being attached to the same nuclear grouping. However, when the size of these nuclear groupings as possibly indicated by the molecular weights of the phenols produced from the two coals is considered, these probabilities for the two coals are not so very different. The nuclear groupings in Edenborn coal must definitely be larger than those in the Illinois coal because the molecular weights of the phenols from Edenborn coal, as calculated from the experimentally determined molecular weights of the methylated phenols, are close to 190, while those from the Illinois coal are only 150. This difference in nuclear size almost compensates for the effect of the difference in oxygen contents when considering the probability of having two oxygen atoms linked to the same nucleus. The higher oxygen content of the Illinois coal is, however, reflected by



the increased productions of phenols, and by the fact that the phenolic oxygen from the Illinois coal represents a larger percentage of the organic oxygen of the coal than is the case with the phenols from Edenborn coal.

The very sharp drop from 23.4 to 2.3 in the percentage of dihydric phenols in the total phenols, as the temperature of carbonization was raised from 400° to 500° C., for the Illinois coal may perhaps be explained on the basis of the instability toward heat of the dihydric phenols. However, this drop in the same temperature interval for the dihydric phenols from Edenborn coal was only from 23.7 to 12.5 per cent. Thus it may be assumed that the dihydric phenols produced from the two coals are different. These phenols are not uniform in their stability toward heat. For example, of the three dihydroxybenzenes, the meta compound is decomposed more rapidly than either of the other isomers, when pyrolyzed at 350° C. (18). If the oxygen distribution in Illinois coal is such that only very thermally unstable dihydric phenols can be produced, then only a very low temperature of carbonization will permit this production to take place.

In Table III is given a comparison between the yields of phenols obtained by the Bureau of Mines (7, 8) using a standard method of analysis (6), and the yields obtained by the method described in this paper. The latter are uniformly higher than the ones given by the standard method, and indicate that appreciable amounts of the phenols originally present in the tar are either destroyed during the standard analysis, or else remain in the pitch, since in the standard method only the phenols in the tar distillate are determined.

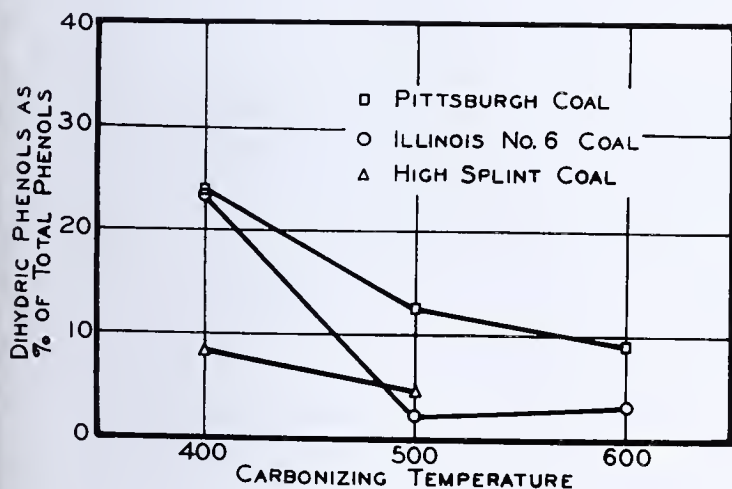


FIGURE 2. COMPOSITION OF PHENOLS AS A FUNCTION OF CARBONIZING TEMPERATURE

This conclusion is open to the objection that the tars made by the Bureau of Mines, and those studied in this investigation, were produced in different types of retorts and therefore are not necessarily similar. For this reason, the phenols in a 500° tar from Edenborn coal were determined by the three methods indicated in Table IV with the results there given. It is clearly shown that the method described in this paper (method 1) does give higher yields of phenols than the standard method (method 3). The results given by method 2 show that most of the decomposition of phenols in the standard method of analysis occurred during the double distillation. Not only was the quantity of phenols in the distillate smaller than that in the crude tar, but the nature of the phenols was also quite different. For example, in the crude tar the phenols had an average molecular weight of 213 and an average of 1.04 hydroxyls per molecule, while in the distillate obtained by the double distillation of the crude tar, they had an average molecular weight of only 149 and an average of 1.02 hydroxyls per molecule.

TABLE III. COMPARISON WITH RESULTS OF STANDARD METHOD OF ANALYSIS

Temperature of carbonization, ° C.	Pittsburgh Coal		Illinois No. 6 Coal	
	500	600	500	600
Tar acids by standard method, % of dry tar	17.4	15.8	29.8	30.0
Phenols by method described in this paper, % of dry tar	23.2	22.8	34.5	38.0

TABLE IV. PHENOLS IN A 500° TAR FROM EDENBORN COAL

	Yield of Phenols, Per Cent of Dry Tar	Average Molecular Weight of Phenols	Average Number of Hydroxyls per Molecule
Method 1 <sup>a</sup>	20.7	213	1.04
Method 2 <sup>b</sup>	15.1	149	1.02
Method 3 <sup>c</sup>	14.2	...	...

<sup>a</sup> Alkali extraction of crude tar in absence of air, followed by methylation of phenolate solution.

<sup>b</sup> Double distillation of crude tar, with distillate treated as in method 1.

<sup>c</sup> Double distillation of crude tar, with tar acids in distillate determined by contraction on shaking with alkali.

## Summary

A method for determining the quantity and average number of hydroxyl groups per molecule of the phenols of a low-temperature tar has been developed and applied to tars made from several bituminous coals at temperatures from 400° to 600° C. The results on a tar from a Pittsburgh Seam coal show that this coal yields tar containing large amounts of dihydric phenols. Results on tars from Illinois No. 6 coal show that this coal can also yield tars containing large quantities of dihydric phenols if the carbonization temperature is kept sufficiently low, but that as the temperature is increased these dihydric phenols are not found in the tar, probably because of their instability toward heat.

Yields of phenols obtained by this method are higher than those obtained by the standard method of analysis, because of decomposition during the double distillation, and probably also because of failure of the phenols in the crude tar to distill at the temperatures reached in the distillation.

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# Barometric Correction Nomograph for Hydrogen Electrode

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MEASUREMENT of pH with certain types of hydrogen electrodes must include a correction for pressure of the hydrogen when it differs from standard one atmosphere of 760 mm. of mercury. The hydrogen pressure may not be standard because of barometer fluctuation, the vapor pressure of solution, hydrostatic head, or other reasons. The correction for these, which Clark (1) calls " $E_{\text{barometer}}$ ", may easily be evaluated, and tables for selected pressures and temperatures are included by Clark (1), Kolthoff (2), and others.

A nomograph, once constructed, offers a convenient method of evaluating this barometric correction for any pressure and temperature within its range; it avoids interpolation in the tables and gives a precision satisfactory for most purposes. Such a nomograph is given here, and as a further convenience, has been made to include the correction for thermal expansion of the mercury in the barometer.

This chart is limited to use when the barometer has a

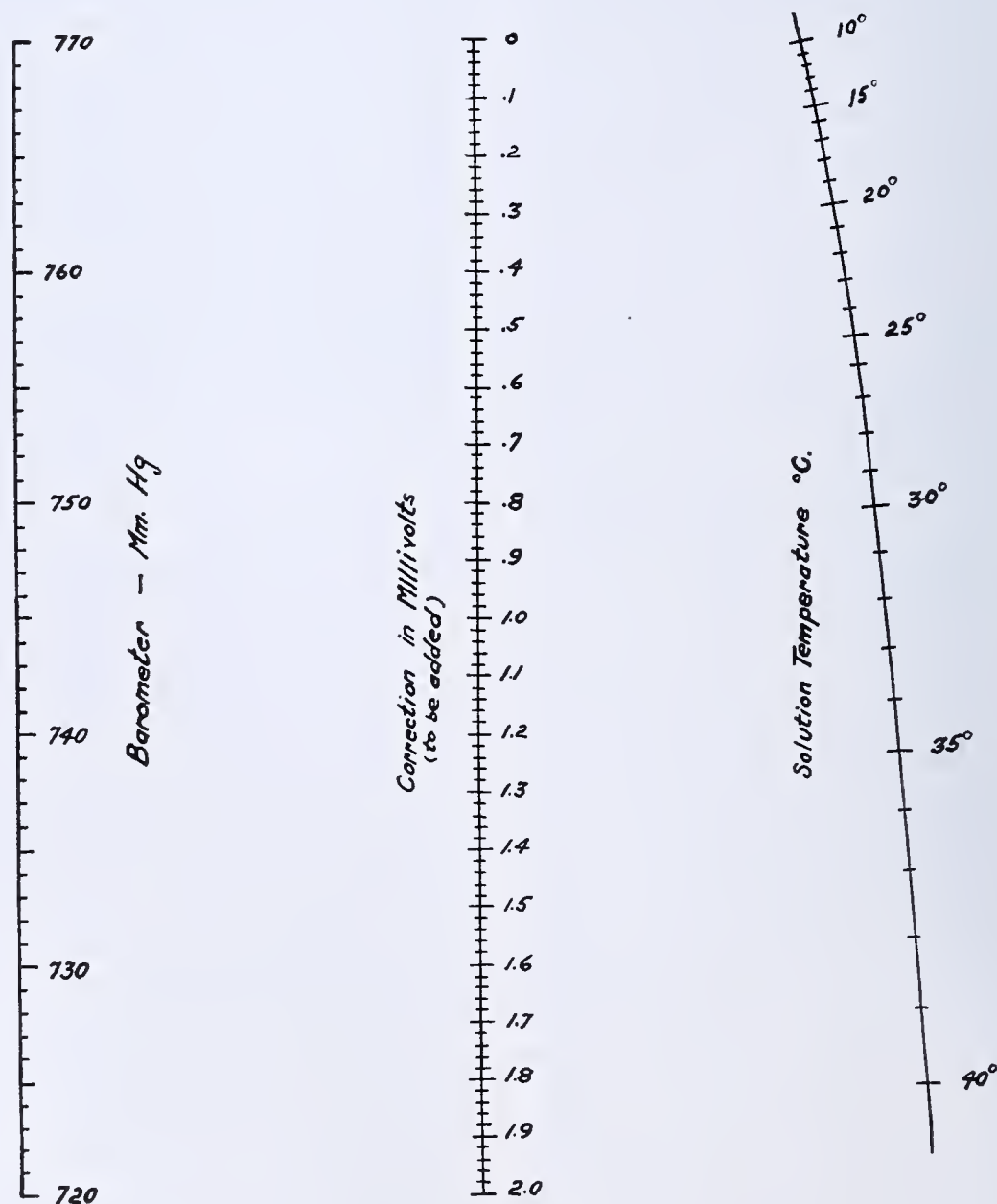
brass scale and is at approximately the temperature of the solution. When the two temperatures are not identical, a small error may be introduced, but the difference must be nearly 5° C. before an error of 0.01 millivolt results. Hydrostatic head and vapor pressure lowering by the solute, neglected here, are usually more important than this.

## Acknowledgment

Data for construction of this nomograph were taken from Clark (1). Thanks are due W. W. Smith and Daniel Rodier for assistance in calculation and drawing.

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NOMOGRAPH



# Determination of Bismuth by the Quinaldine Salt of Iodobismuthous Acid

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IT HAS long been known that many organic bases, such as quinoline (4), quinine (3) and the like, form, in the presence of iodides and certain metals, compounds which because of their characteristic colors are suitable for the detection of these metals. However, very few of these organic bases have been investigated from a quantitative standpoint. Berg and Wurm (2) were able to determine cadmium and bismuth, as well as separate these metals from others, by the use of naphthoquinoline and *o*-hydroxyquinoline. The latter reagent was also studied by Kolthoff and Griffith (6). In view of the many compounds available, some of which are more basic than *o*-hydroxyquinoline, it seemed advisable to investigate this field further.

Quinaldine was found to give good results in the determination of bismuth. In the presence of dilute sulfuric acid and excess of potassium iodide, the bismuth is completely precipitated by this reagent, and may then be readily determined volumetrically, through the relationship of four iodides to one bismuth. Many other ions, both metallic and nonmetallic, either do not affect the determination at all or may be readily prevented from interfering.

## Determination of Bismuth

**MATERIALS USED.** The quinaldine used was obtained from the Eastman Kodak Company and used without further purification. Pure solutions of bismuth nitrate were prepared and standardized both as the phosphate and the oxide. The potassium iodate solutions were prepared from the pure salt by direct weighing. Solutions of potassium iodate are very stable, according to Jamieson (5), but as a further check were occasionally standardized against pure, dry potassium iodide. No significant change was found in any case. All other reagents used were of C. P. grade.

**PROCEDURE.** The sample (containing about 0.03 gram of bismuth) is dissolved in sulfuric acid and diluted to about 200 cc., and the acidity is adjusted to about 1 *N*. After the addition of 15 cc. of a 10 per cent sodium sulfite solution, bismuth is precipitated by the dropwise addition, with stirring, of 20 cc. of a solution containing 150 cc. of quinaldine, 50 cc. of concentrated sulfuric acid, and 75 grams of potassium iodide per liter. After being allowed to settle, which requires 15 to 20 minutes if well stirred, the red precipitate is filtered with suction on a Gooch filter or a fritted-glass filter cell. The precipitate may stand several hours before filtering without apparent decomposition, but preferably not overnight. It is first washed with 40 to 50 cc. of a solution of 35 cc. of quinaldine, 15 cc. of concentrated sulfuric acid, and about 0.8 gram of potassium iodide per liter. As washing with water must be avoided to prevent decomposition of the precipitate, the small amount of excess iodide left by the first wash solution is removed by washing with 30 cc. of a solution of 10 per cent acetone in *N* dibutyl ether.

The crucible containing the well-washed precipitate is then transferred to a beaker and about 100 cc. of a 5 per cent sodium hydroxide solution are added. To ensure complete decomposition of the precipitate the solution is heated almost to boiling for about 20 minutes, after which it is cooled and neutralized with concentrated hydrochloric acid, and an excess of 10 cc. is added. After adding 8 cc. of a 0.5 *M* potassium cyanide solution, the iodide is titrated to iodine cyanide according to Lang's method (7). Each milliliter of the 0.1 *N* (0.025 *M*) potassium iodate solution is equivalent to 0.002612 gram of bismuth.

An average error of about 0.30 per cent was found in analyzing pure bismuth samples by this method.

## Separation of Bismuth from Mixtures

With slight modifications the procedure described above may be used for the determination of bismuth in the presence

of a considerable number of other metallic ions and many of the common anions.

**ANTIMONY.** In the case of antimony a synthetic sample was prepared containing 0.044 gram of antimony sulfate and 0.0303 gram of bismuth. Before precipitating the bismuth about 4 grams of ammonium tartrate were added and the bismuth was determined as described above. The average value for six such determinations was 0.0304 gram of bismuth, with an average error of 0.29 per cent.

**LEAD.** To the standard bismuth solution, containing 0.0303 gram of bismuth, was added 0.08 gram of lead nitrate. The bismuth may be precipitated directly, after the usual dilution and acidification with sulfuric acid, but it was found to be slightly more accurate to remove the lead first. This was done by adding excess sodium sulfate and filtering off the precipitated lead sulfate. The average of six such determinations was 0.0303 gram of bismuth, with an average error of 0.27 per cent.

**CADMIUM.** A composite sample, containing 0.0303 gram of bismuth and 0.08 gram of cadmium chloride, was analyzed for bismuth after the addition of 5 cc. of pyridine. The average of six analyses was 0.0303 gram of bismuth, with an average error of 0.29 per cent.

**COPPER.** In this case a sample was prepared to consist of 0.0303 gram of bismuth and 0.075 gram of cupric sulfate. Before precipitating the bismuth, 15 cc. of a 10 per cent sodium sulfite solution were added. The average of eleven such determinations was 0.0303 gram of bismuth, with an average error of 0.14 per cent.

**IRON.** The separation of 0.0303 gram of bismuth from 0.22 gram of ferric nitrate offered no difficulty. The bismuth was precipitated in the presence of about 3 grams of sodium sulfite. Seven such determinations gave an average value of 0.0303 gram of bismuth, with an average error of 0.18 per cent.

**TIN.** The determination of bismuth in the presence of stannous tin gave no trouble. In this case the average of eight determinations of 0.0303 gram of bismuth in the presence of 0.80 gram of stannous chloride was 0.0303 gram of bismuth. If the tin was present in the stannic form, it was found best to add about 15 cc. of 10 per cent sodium sulfite solution prior to precipitation of the bismuth. The average of six determinations of 0.0303 gram of bismuth in the presence of 0.90 gram of stannic chloride was 0.0305 gram of bismuth, with an average error of 0.43 per cent.

**ARSENITE.** In this case 0.0303 gram of bismuth was determined in the presence of 0.04 gram of arsenic trioxide, proceeding exactly as for a pure bismuth sample. The average of six determinations was 0.0304 gram of bismuth, with an average error of 0.30 per cent.

**ARSENATE.** The determination of 0.0303 gram of bismuth in the presence of 0.036 gram of arsenic acid presented no difficulty. Proceeding as for a pure bismuth sample, the average of six analyses was 0.0303 gram of bismuth, with an average error of 0.05 per cent.

**PHOSPHATE.** The procedure in the presence of phosphate was the same as for a pure bismuth sample, with one exception. Here the acidity was adjusted to about 4 *N*, in order to prevent the precipitation of any bismuth as the phosphate. Under these conditions the average of six determinations of 0.0303 gram of bismuth in the presence of 0.20 gram of sodium orthophosphate was 0.0303 gram of bismuth, with an average error of 0.10 per cent.

**NICKEL, CHROMIUM, COBALT, MANGANESE, CALCIUM, BERYLLIUM, URANYL, ALUMINUM, TITANIUM, AND BARIUM.** A synthetic sample was prepared containing 0.0303 gram of bismuth and 0.10 gram of chromium nitrate, 0.06 gram of manganese sulfate, 0.05 gram of cobalt sulfate, 0.08 gram of calcium nitrate, 0.16 gram of beryllium carbonate, 0.03 gram of uranyl acetate, 0.05 gram of nickel sulfate, 0.125 gram of aluminum sulfate, 0.08 gram of titanium sulfate, and 0.04 gram of barium nitrate. The bismuth was then precipitated and determined exactly as in a pure sample. The average of seven such determinations was 0.0303 gram of bismuth, with an average error of 0.05 per cent.

**ANTIMONY, ZINC, ALUMINUM, NICKEL, SODIUM, AND POTASSIUM.** A composite sample was prepared to contain 0.0303 gram



of bismuth and 0.02 gram each of antimony, zinc, aluminum, nickel, sodium, and potassium, each present as the sulfate. Before precipitation of the bismuth, 4 grams of ammonium tartrate were added and the determination was completed as usual. The average of five such analyses was 0.0306 gram of bismuth, with an average error of 0.60 per cent.

**LEAD, ANTIMONY, TIN, AND COPPER.** A synthetic lead-base bearing metal was prepared by adding 0.0303 gram of bismuth to 0.8 gram of lead, 0.1 gram of tin, 0.1 gram of antimony, and 0.02 gram of copper. The sample was dissolved in sulfuric acid, the lead sulfate was filtered off, 4 grams of ammonium tartrate and 10 cc. of 10 per cent sodium sulfite solution were added, and the bismuth was precipitated and determined as usual. The average of three such determinations was 0.0302 gram of bismuth, and the average error was 0.22 per cent.

### Determination of Very Small Amounts of Bismuth

For the determination of very small amounts of bismuth the procedure previously outlined is slightly modified.

The precipitation of the bismuth is done in the same manner, except that smaller amounts of quinaldine and potassium iodide are used. The precipitate is filtered, washed, and dissolved as usual, but the titration in this case is done with 0.01 *N* (0.0025 *M*) potassium iodate solution (1 cc. = 0.0002612 gram of bismuth). The iodide is titrated to iodine chloride according to Andrews' method (1), which, in accordance with the findings of Kolthoff and Griffith (6) gives better results. A microburet was used in these titrations. The average of twelve samples, each containing 0.00032 gram of bismuth, was 0.00033 gram, with an average error of 2.3 per cent.

### Interfering Ions

In the presence of any appreciable amount of chloride the results were generally low, in all probability because of a partial replacement of the iodide in the precipitate by chloride.

The largest amount of chloride present in any of the determinations reported was represented by 0.90 gram of stannic chloride.

Bismuth could not be determined in the presence of silver and mercury by this method.

### Summary

A new method for the determination of bismuth, which involves the precipitation of bismuth as the quinaldine salt of iodobismuthous acid, is described. This method is applicable to amounts of bismuth as low as 0.3 mg.

By this method bismuth may be separated and determined in the presence of lead, antimony, tin, cadmium, copper, iron, chromium, manganese, cobalt, calcium, barium, uranyl, nickel, beryllium, aluminum, titanium, zinc, sodium, potassium, arsenite, arsenate, and phosphate.

The determination may be successfully carried out in acidities ranging from 2.5 to 10 per cent of sulfuric acid by volume.

The determination of bismuth in the presence of mercury and silver is not feasible. High concentrations of chlorides lead to low results.

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## Direct Determination of Alumina in Certain Silicates

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THE direct determination of alumina in silicates, without regard to the other constituents, is often of considerable interest to the analytical chemist. Under ordinary conditions the determination follows a preliminary separation of silica by the conventional alkali carbonate—mineral acid solution—double dehydration procedure. If silica is not desired and volumetric means of evaluating the alumina content are to be used, single dehydrations suffice, provided that the acid-insoluble oxychlorides of the  $R_2O_3$  group are added to the main silica filtrate. This procedure is extremely lengthy.

Knowles and Redmond (10) used a Berzelius decomposition for the removal of silica in feldspar, ultimately determining aluminum volumetrically as quinolate. Certain precautions are necessary to ensure complete removal of hydrofluoric acid, for the presence of this acid, even in minor quantities, prevents the complete precipitation of the aluminum complex. Excellent results are to be obtained by the use of this procedure.

Stuchert and Meier (18), who claim that the Berzelius decomposition leads to low results, modified the method to some extent. The sample is evaporated with hydrofluoric acid alone, and the residue is heated gently to remove the free acid and finally taken into solution by fusion with potassium pyrosulfate. The fused mass is dissolved in 1 to 10 sulfuric acid and the aluminum is determined as quinolate. Experience with the method in the author's laboratory indicated a partial loss of aluminum, and

there was some evidence of incomplete decomposition of the more refractory materials.

Procedures dependent upon removal of silica as silicon tetrafluoride find application only when the material under analysis is completely soluble in hydrofluoric acid or hydrofluoric-sulfuric acid. Ideal conditions for the determination of aluminum in silicates would be based upon (1) complete and rapid decomposition of the sample, (2) a volumetric determination, and (3) the presence of silica.

Inasmuch as silica does not form a complex with 8-hydroxyquinoline in the absence of a molybdic acid salt, it was thought that the aluminum could be precipitated directly from the acid solution of the alkali carbonate melt, as was first suggested by Krinke (12) for the determination of aluminum in glasses. Unfortunately, upon adjustment of the pH to the point of precipitation of aluminum as quinolate, the separation of silica presented a particularly difficult filtration problem and this mode of attack was abandoned. This separation of silica appears to be a function of the amount of aluminum present in the sample under analysis.

The rapid reaction with molten alkali and the amphoteric nature of aluminum oxide suggested an initial decomposition based upon fusion with potassium or sodium hydroxide, fol-



lowed by acidification to redissolve the aluminum hydroxide and precipitation of aluminum as the quinolate. Most silicates proved amenable to this fusion treatment, but separation of the silica, upon acidification of the water solution of the alkali melt, again caused difficulty.

Taking advantage of the property that 8-hydroxyquinoline removes the complex-forming metals from their insoluble salts (9), a method based upon the alkali fusion discussed above was devised. This involved fusion of the sample with an alkali flux in a nickel beaker, solution of the fused mass in water, and subsequent boiling to precipitate nickelic and ferric hydroxides. These were removed by filtration, and the clear solution was treated with an excess of an acetic acid solution of the reagent, the aluminum complex being soluble in the highly alkaline original solution. Hydrochloric acid was added, through the stage of complete precipitation, continuing until practically all of the precipitate was dissolved. The pH was finally adjusted with ammonium acetate. For some reason the presence of the organic reagent allows a greater acidity, before precipitation of silica, than does the modification previously outlined. This procedure was productive of excellent results when working with materials having a relatively low iron content—0.1 per cent or less.

Application of the method to the analyses of materials of relatively high iron content soon made it apparent that a portion of both the nickel and iron had escaped precipitation as hydrous oxide and was to be found in the filtrate. Quantitative determinations of the iron indicated that the amount escaping separation, probably as an alkali ferrate, was by no means constant. Previous work in the author's laboratory did not substantiate the broad statement of Stuchert and Meier (18) that iron to the extent of 3 per cent of the aluminum content is without effect upon the final results for aluminum. (Unpublished results of H. R. Shell show that ferric iron, introduced as ferric chloride into feldspar samples, precipitated quantitatively as the quinolate with the exception of a constant amount of 0.09 mg. which escaped as colloid. This value proved to be true for ferric oxide additions of 0.1 to 5.0 mg.)

The problem of iron interference presents itself most forcibly in the analysis of clays, unprocessed nepheline syenites, certain lepidolites, and other silicates most often bearing high-iron accessory minerals. Corrections based upon the ferric iron content of the alkali filtrate are not permissible, for the analyst has no assurance that the iron is to be found completely in the ferric condition at the time of precipitation of aluminum with 8-hydroxyquinoline. The analyst has two alternatives for the elimination of this difficulty: complete removal of iron before attempting precipitation of aluminum or the formation of a soluble iron complex which will inhibit the iron-quinolate reaction.

Both Haslam (6) and Skinner (17) remove iron as the sulfide from alkali tartrate solutions and Skinner has used this method as a basis for the determination of iron in glass sands. Fainberg and Tel (4) reduce the iron with sodium thiosulfate and form the stable alkali ferrocyanide by the addition of potassium cyanide. Heczko (7) uses a similar method, substituting hydrogen sulfide as the reductant. By either of the latter two methods aluminum can be determined in the presence of both silica and iron. Each, however, has the disadvantage inherent in the use of potassium cyanide in slightly acid solution.

Separations based upon controlled acidity (15, 20) or upon the formation of aluminum complexes with salicylic (1), malonic (2), or oxalic acid (21) all depend upon precipitation of iron as quinolate in acid solution and in some of the latter cases the carboxylic acid must be completely removed before the aluminum quinolate can be precipitated. These methods and their greatest usefulness in the separation of iron when

in relatively greater proportion than the aluminum. None would find application in the present instance because of the possibility of separation of silica at the optimum pH for the iron separation.

Churchill and Bridges (3) state that iron must be in the ferric condition before precipitation as quinolate can be accomplished and they resort to an oxidation before precipitation of iron and aluminum preliminary to the determination of beryllium in aluminum-beryllium alloys. It appeared that on reducing the iron to the ferrous state, precipitation of iron as quinolate would be prevented and reliable values for alumina would result. The ferrous salts proved unstable, however, as was shown by Willard and Tang (19), and precipitation of ferric quinolate invariably took place upon exposure of the previously reduced solutions to the atmosphere.

Ferrari (5) has recently shown that the ferrous complex of  $\alpha, \alpha'$ -bipyridine,  $\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3\text{X}_2$ , where X is a monovalent acid radical, is so stable that the iron cannot be removed from this complex as the hydroxide, ferricyanide, or sulfide. Hill (8) has shown that, though the complex is easily dissociated in mineral acid solutions of high concentration, it is stable in the pH range of 3.5 to 8.5. Saywell and Cunningham (16) used the analogous complex-forming properties of *o*-phenanthroline for the same purpose, while Mayr and Gebauer (13) proposed the use of thioglycolic acid in ammoniacal solution to prevent the precipitation of iron as hydroxide. In all these the iron is previously reduced with sulfurous acid or an organic reductant such as hydroxylamine hydrochloride. These data indicated that an inhibition of the ferric quinolate precipitation might be possible if the iron were held as the ferrous complex. Early experimental trials proved this premise to be true with either *o*-phenanthroline or  $\alpha, \alpha'$ -bipyridine. The use of thioglycolic acid was not studied in this investigation. *o*-Phenanthroline may have some advantage, in the direction of greater stability (14), over the  $\alpha, \alpha'$ -bipyridine reagent.

### Reagents and Equipment

c. p. pellets of sodium hydroxide are satisfactory.

Dissolve 100 grams of 8-hydroxyquinoline (Eastman Kodak Co.) in 200 ml. of glacial acetic acid and add to 3 liters of water previously heated to 80° C. Filter if necessary, and dilute to 4 liters.

Ammonium Acetate Buffer. Three grams of the salt per 10 ml. of solution.

One gram of *o*-phenanthroline or  $\alpha, \alpha'$ -bipyridine hydrochloride in 100 ml. of 6 *N* hydrochloric acid.

A saturated solution of hydroxylamine hydrochloride in water.

Potassium Bromate-Bromide, 0.25 *N*. Dissolve 6.97 grams of potassium bromate and 25 grams of potassium bromide in 1000 ml. of water. Standardize against sodium thiosulfate or by the method described by the author (11).

Sodium Thiosulfate, 0.10 *N*. Dissolve 25 grams of sodium thiosulfate pentahydrate and 1 gram of boric acid in 1000 ml. of sterile water. Store in a dark bottle. Standardize against iodine or by the method previously described (11).

Potassium Iodide, 60 per cent. Dissolve 60 grams of U. S. P. potassium iodide in 100 ml. of water.

Add 5 grams of a cold suspension of soluble starch to 500 ml. of boiling water. When cool add 15 grams of potassium iodide and 5 grams of sodium hydroxide in 25 ml. of water. Store in a dark bottle.

A 250-ml. nickel beaker of the same shape as the Griffin low-form glass beaker is suitable.

### Procedure

A quantity of the dried (105° C.) and finely ground (200-mesh) sample sufficient to produce between 10 and 30 mg. of alumina is transferred to a nickel beaker containing at least ten times the sample weight of previously fused sodium hydroxide. The beaker is heated, gently at first, to complete solution of the sample in the flux and finally at 400° to 500° C. for a few moments; the beaker should show a dull red through the melt. The beaker is covered, and cooled, and 100 ml. of water are added. Heating to solution of the fused mass is followed by



TABLE I. DETERMINATION OF ALUMINA

Sample	Material	Al <sub>2</sub> O <sub>3</sub> Present Mg. <sup>a</sup>	Al <sub>2</sub> O <sub>3</sub> Found Mg.	Differ- ence Mg.	Remarks
1	Feldspar No. 70	18.03 <sup>b</sup>	18.03	±0.00	
2	Feldspar No. 99	19.06 <sup>b</sup>	19.06	±0.00	
3	Feldspar	15.60	15.60	±0.00	
4	Feldspar	18.20	18.20	±0.00	
5	Cornwall stone <sup>c</sup>	15.15	15.17	+0.02	1.2% F present
6	Lepidolite	13.40	13.40	±0.00	3.4% F present
7	Lepidolite <sup>c</sup>	13.64	13.64	±0.00	2.2% F present 0.4% MnO <sub>2</sub> present
8	China clay <sup>c</sup>	17.50	17.48	-0.02	0.2% TiO <sub>2</sub> present
9	China clay <sup>c</sup>	18.10	18.10	±0.00	0.1% TiO <sub>2</sub> present
10	Beryl	11.40	11.36	-0.04	
11	Nepheline syenite <sup>c</sup>	13.00	13.00	±0.00	
12	Nepheline syenite <sup>c</sup>	11.10	11.10	±0.00	
14	Kyanite <sup>c</sup>	30.03	29.97	-0.06	
15	Glass sand	10.71	10.71	±0.00	
16	Potter's flint <sup>c</sup>	10.22	10.22	±0.00	
17	Aplite <sup>c</sup>	23.14	23.14	±0.00	
18	Spodumene	14.84	14.84	±0.00	
19	Amblygonite	11.03	11.06	+0.03	3.5% F present
20	Burned refractory <sup>c</sup>	37.67 <sup>b</sup>	37.69	+0.02	2.2% TiO <sub>2</sub> present

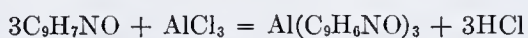
<sup>a</sup> Values obtained in ordinary manner after removal of silica and recovery of nonvolatile matter.

<sup>b</sup> National Bureau of Standards recommended value.

<sup>c</sup> Correction for iron applied after precipitation of iron and alumina on basis of: Total ferric iron—0.1 mg. × 0.6 (10).

boiling for a few moments to coagulate the precipitated nickelic and ferric hydroxides. The solution is filtered through a Whatman No. 41H paper into a 250-ml. beaker. The nickel beaker is polished and the paper washed well with hot water. The paper is discarded.

The filtrate is treated with 15 ml. of 8-hydroxyquinoline solution and the precipitate first formed is dissolved by stirring. Hydrochloric acid is now added, drop by drop, while stirring, through the stage of apparent complete precipitation, continuing until the precipitate is completely dissolved and the solution is distinctly acid. During this preliminary precipitation, observation of the color of the precipitate—ferric quinolate is distinctly green—will indicate whether the iron is present in sufficient quantity to necessitate preventing its precipitation. If this is required, sufficient hydroxylamine hydrochloride solution is added to effect reduction of ferric iron and the solution is heated to 80° to 90° C. An excess of  $\alpha, \alpha'$ -bipyridine hydrochloride or *o*-phenanthroline hydrochloride solution is added and the aluminum is precipitated by the addition of ammonium acetate buffer solution, 10 ml. in excess of that required for complete precipitation. The precipitation reaction is as follows:



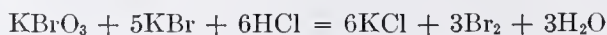
The suspension is coagulated by stirring if the iron quinolate reaction has been inhibited (the ferrous *o*-phenanthroline or ferrous bipyridine complex is dissociated by boiling) or by boiling if no effort was made to prevent the iron precipitation, and filtered through a Whatman No. 41H paper. The beaker is rinsed and the residue washed with cold water, the filtrate being discarded. The residue is dissolved directly from the paper with boiling 1 to 1 hydrochloric acid, catching the filtrate in the beaker in which the original precipitation was made. The paper is washed several times with boiling 5 per cent hydrochloric acid and discarded. The solution of the residue in hydrochloric acid again produces 8-hydroxyquinoline according to the reaction



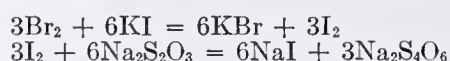
The filtrate containing the 8-hydroxyquinoline is made to 125 ml. with water and a measured excess of potassium bromate-bromide solution is added while stirring. The following reaction takes place:



The excess bromate-bromide reacts:



The addition of an excess (1 ml. is sufficient) of potassium iodide solution converts the free bromine to free iodine and this excess is measured by titration with sodium thiosulfate solution to a starch end point



This is calculated to percentage of alumina.

The results obtained by the procedure described are shown in Table I.

## Discussion of Results

This procedure proved satisfactory for all the materials covered in Table I, though certain modifications were at times necessary.

The analyst can easily recognize the  $\alpha, \alpha'$ -bipyridine or *o*-phenanthroline requirements of the iron present as quinolate during the initial precipitation. Very little excess over the reagent required to satisfy the formula  $\text{Fe}(\text{C}_{10}\text{H}_8\text{N})_3\text{Cl}_2$  was necessary. In no case was any iron found in the aluminum quinolate residue.

Among the other metals which form quinolates and might interfere with the determination of aluminum as quinolate are titanium, zirconium, manganese, uranium, vanadium, and magnesium. Titanium and zirconium in the presence of iron will separate quantitatively as the hydroxide and will be found in the initial residue. Manganese separates as manganese dioxide in alkaline solution. Uranium and vanadium will probably be found with the aluminum, unless a second precipitation of the aluminum quinolate is made in a solution containing hydrogen peroxide. Magnesium forms the quinolate only in ammoniacal solution and no interference of this metal need be anticipated if the aluminum is precipitated under the conditions described.

Although the same basic procedure was used on all the samples covered in the study, certain changes in sample—flux ratio and the temperature cycle—were sometimes necessary.

**FELDSPAR.** The feldspars studied were all relatively free of iron. The sample (100 mg.) can be brought into solution with 1 gram of sodium hydroxide but hydrolysis of the aluminum hydroxide sometimes takes place unless more than 1.5 grams of the flux is used.

**CORNWALL STONE.** The Cornwall stone fused readily with 1.5 grams of sodium hydroxide when 100-mg. samples were used and the iron quinolate reaction was inhibited.

**LEPIDOLITE.** At least 2 grams of the flux are required for each 50 mg. of sample. Sample 7 proved high in iron and the reaction was inhibited.

**CHINA CLAY.** Because of its light, fluffy nature, the use of alcoholic sodium hydroxide was required. The sample and flux were moistened with alcohol and thoroughly dried before fusion. The flux-sample ratio was 40 to 1.

**BERYL** reacted in the same manner as the feldspar sample.

**NEPHELINE SYENITE.** Samples 11 and 12 represent unprocessed materials originally containing 4.72 and 3.70 per cent of ferric oxide, respectively. The ferric oxide contents of the alkali filtrates were 0.97 and 0.84 per cent, respectively, and necessitated the *o*-phenanthroline or bipyridine treatment. Because of the high alumina content at least 2 grams of flux are required for each 100 mg. of sample. Samples of this material which had been previously processed reacted like feldspar samples, though a greater amount of flux would prove advantageous in preventing hydrolysis.

**KYANITE.** A flux-sample ratio of 40 to 1 was required and it was found necessary to heat at a higher temperature and for a longer period to ensure complete decomposition.

**GLASS SAND AND POTTER'S FLINT** are similar in chemical composition. One gram of the sample and 5 grams of flux were used in either case.

**APLITE** was easily fused with 2 grams of flux per 100 mg. of sample.

**SPODUMENE.** A flux-sample ratio of 20 to 1 proved suitable.

**AMBLYGONITE** can be effectively brought into solution with a flux-sample ratio of 20 to 1.

**BURNED REFRACTORY.** A flux-sample ratio of 100 to 1 was required and it was found necessary to heat at a higher temperature for a longer period of time to ensure complete decomposition.

## Conclusions

The determination of alumina as the quinolate in the presence of silica and iron is feasible and the method outlined offers definite advantages over those ordinarily employed for



this purpose. The method is economical because no platinum or extremely high temperatures are required and the reagent cost is low.

### Acknowledgment

The author is indebted to Thomas C. Carson, Jr., for many helpful suggestions and analytical data.

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# Determining Riboflavin in Dried Milk Products

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SEVERAL physico-chemical methods have been proposed for the determination of riboflavin, all of which may be grouped under one of three headings:

1. Preparation of a derivative whose solubility properties differ markedly from those of riboflavin, and determination of the color of the resulting solution (6).
2. Direct measurement of the color of riboflavin solutions (3).
3. Measurement of the fluorescence of riboflavin solutions (1).

By preparing a derivative, it is possible to separate the pigment from other colored substances which may accompany riboflavin in extracts of natural products. Thus, riboflavin is a water-soluble pigment, whereas lumiflavin is soluble in chloroform. However, the preparation of lumiflavin is accompanied by large losses (4, 6).

The direct measurement of the color of extracts of biological materials is subject to error due to the presence of other colored substances. This method may be somewhat refined (4) by controlled oxidation of these impurities. However, with more vigorous treatment, riboflavin is also destroyed, so that at times it is impossible to purify the extracts completely.

The determination of fluorescence is complicated by a number of factors, two of which are most obvious: The intensity of fluorescence is not a linear function of the concentration of riboflavin but passes through a maximum with increasing concentration (2). Extracts of biological materials contain blue (4) and white (7) fluorescing substances which interfere with the accurate determination of the green fluorescence due to riboflavin.

Since this vitamin has received increased attention during the past few years, it is apparent that a rapid, quantitative method of estimating riboflavin is still needed. Such a method was developed by the authors two years ago and has been in constant use since that time.

### Principle of the Method

An extract of dried milk products is prepared and freed from unstable colored impurities by controlled oxidation. Light of the frequencies which are absorbed by riboflavin is passed

through the extract and the amount of absorption is determined with a photoelectric photometer. The riboflavin is then reduced to the leuco form and the measurement repeated to determine the amount of light absorbed by impurities. The concentration of riboflavin is calculated from the difference between these two readings.

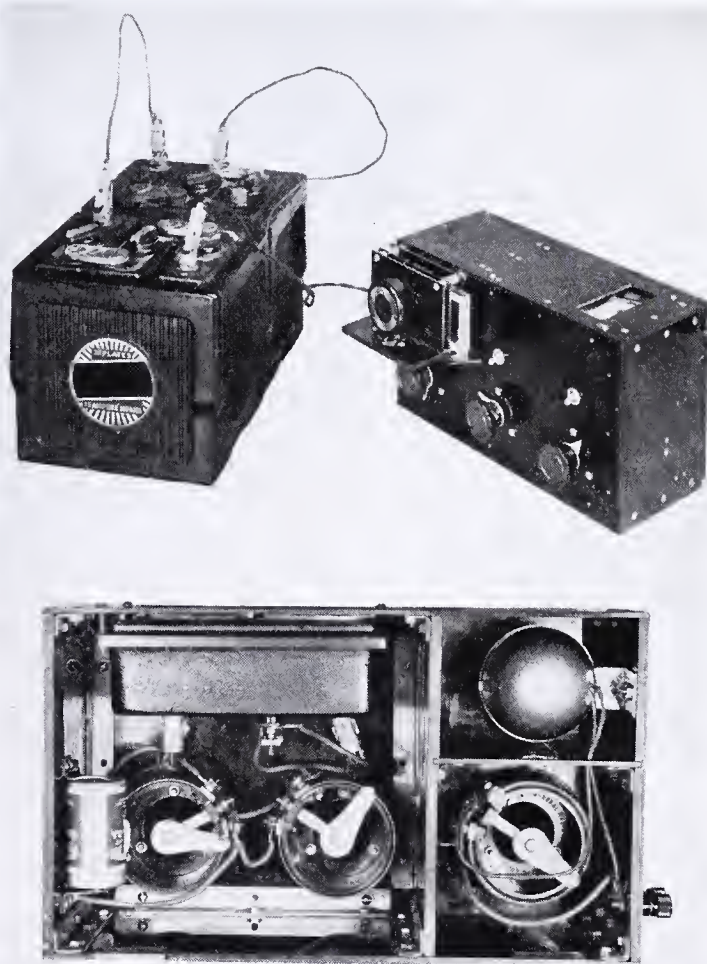


FIGURE 1. EXTERIOR AND INTERIOR VIEWS OF PHOTOMETER

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### Apparatus

The photoelectric photometer, constructed for this work, employs a single photocell of the blocking-layer type. The zero-potential circuit, proposed by Wood (9) for use with these cells, has made it possible to obtain a current that is in exact proportion to the light intensity.

Views of the photometer are presented in Figure 1. The rear wall of the Bakelite box is placed on hinges, so that all parts are readily accessible.

A schematic wiring diagram is given in Figure 2.  $M$  is a microammeter with internal resistance of 150 ohms and critical damping resistance of 1000 ohms.  $B$  is a flashlight dry cell.  $K_1$  and  $K_2$  are contact keys, the former for controlling the dry cell and the latter for short-circuiting the photocell.  $R_1$ ,  $R_2$ , and  $R_3$  are potentiometer rheostats of 10,000, 1000, and 5 ohms' resistance, respectively.  $P$  is a blocking-layer photocell.  $D_1$ ,  $D_2$ ,  $D_3$ , and  $D_4$  are constant-aperture diaphragms which also serve to hold filters  $F_1$  and  $F_2$  in place. The light source,  $L$ , is a 9.6-volt flashlight bulb. Two 6-volt storage batteries,  $S$ , furnish the current for the light. A convenient type of absorption cell,  $A$ , is of 20-ml. capacity with a path length of 1 cm.

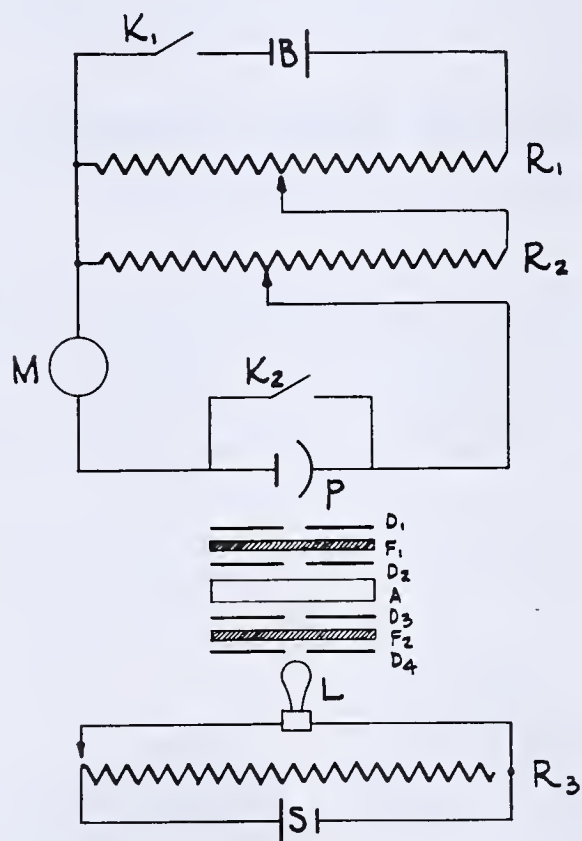


FIGURE 2. WIRING DIAGRAM

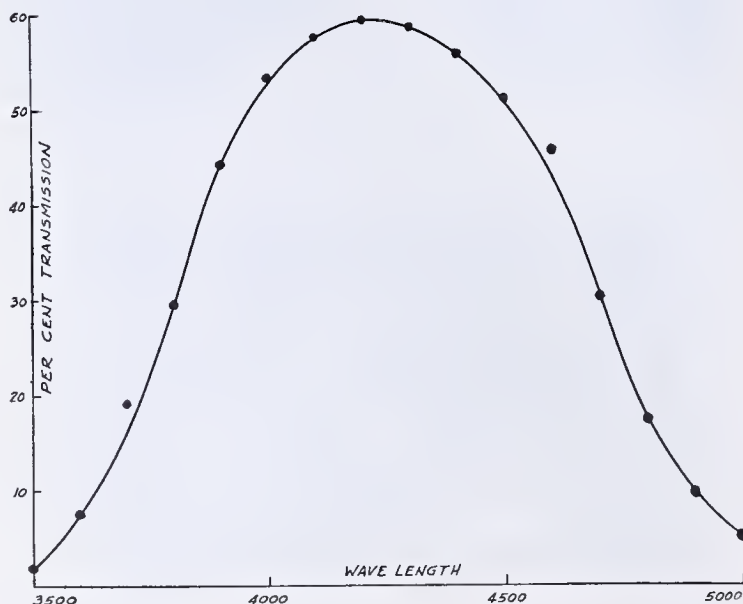


FIGURE 3. TRANSMISSION CURVE

The intense beam of light obtained from the flashlight bulb is rendered parallel by means of a reflector. Since the efficiency of the reflector has been found to decrease gradually over a period of months, 6, 8, 10, or 12 volts may be tapped off from the storage batteries to obtain the proper light intensity. The final adjustment is made by means of the 5-ohm rheostat.

Circular holes, 2.5 cm. (1 inch) in diameter, are cut in the partitions which support the filters, so that the beam striking the photocell is essentially parallel light perpendicular to its surface. In order to limit the illumination to light of the desired frequencies a set of H. R. lantern blue filters (Corning Glass Works, Corning, N. Y.) was selected. The transmission curve of these filters is given in Figure 3. One filter is placed between the light and the absorption cell, so that only light of the desired wave lengths is transmitted to the solution. This procedure reduces unnecessary heating of the solution. An identical filter is placed between the absorption cell and the photocell to filter out fluorescence caused by illumination of the sample. Even with low light intensities, certain materials, such as riboflavin, produce sufficient light to influence the reading. This precaution is particularly important when working with blue light, since the photocell is more sensitive to the longer wave lengths produced by fluorescing materials than to the original light.

### Operation of the Photometer

An absorption cell filled with water, or other solvent to be used for the unknown, is placed in the path of the light. With switches  $K_1$  and  $K_2$  closed, the current from the dry cell is adjusted to give a full-scale deflection. This procedure enables one to predetermine the voltage required to balance the fall of potential across the ammeter when the photocell is producing a full-scale deflection. Switch  $K_2$  is then opened and the light intensity is adjusted by means of the resistance in series with the lamp until a full-scale deflection is again obtained. If this has been properly done there will be no change in deflection upon opening and closing  $K_2$ .

Another advantage in the present circuit is that with the photocell short-circuited, an unknown solution may be substituted for the solvent without causing the usual violent fluctuation of the ammeter. The current from the dry cell is reduced to approximately the reading expected and  $K_2$  is opened. The direction in which the needle is deflected will indicate whether the applied voltage is too large or too small.  $K_2$  is then closed and the current from the dry cell is modified accordingly. In this way the applied voltage is again adjusted to equal exactly the fall of potential across the am-

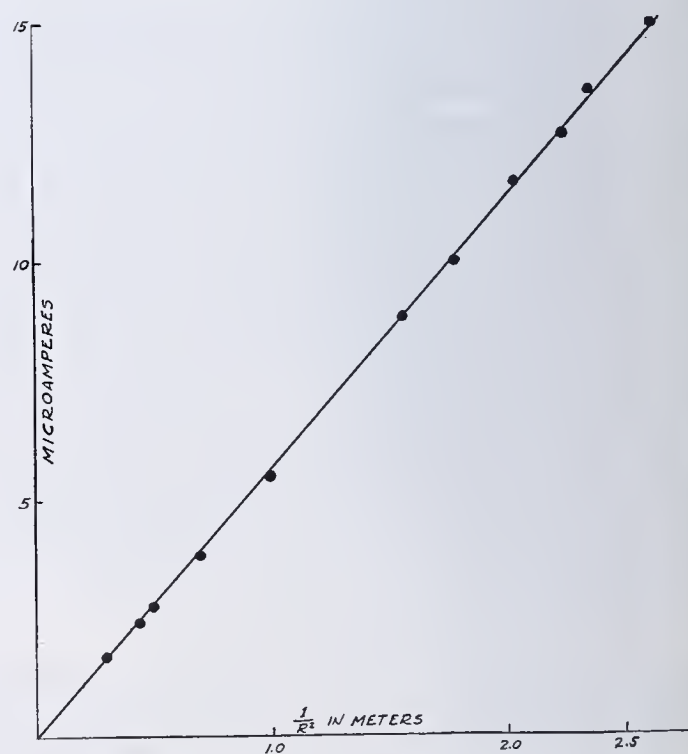


FIGURE 4. CALIBRATION CURVE



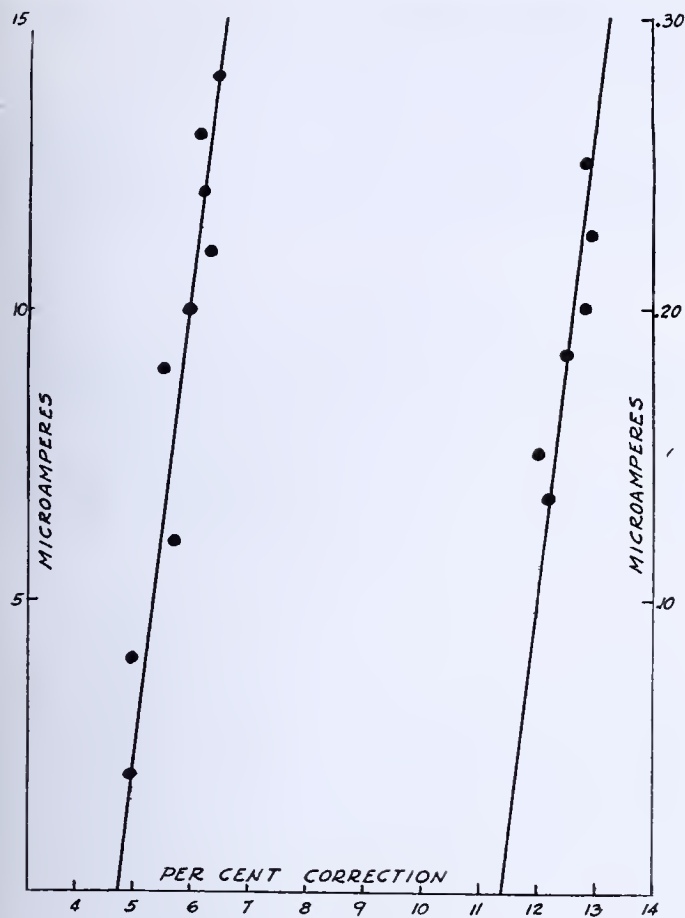


FIGURE 5. CORRECTION FACTOR

meter, so that no change in deflection is obtained upon opening or closing  $K_2$ .

To demonstrate that this instrument would give a linear response to varying light intensities, observations were made as a light bulb was moved along an optical bench. The current obtained should be inversely proportional to the square of the distance separating the photocell from the light. These results are presented in Figure 4 and demonstrate that, with the zero-potential circuit, the current obtained from the photocell is a linear function of the light intensity.

The difference between these results and the readings which are obtained by connecting the photocell directly to the meter is demonstrated in Figure 5. Readings were made first in the usual manner and then with the zero-potential circuit and the difference between the two readings was calculated in per cent of the correct reading. The dependence of this correction upon the internal resistance of the meter is also shown in Figure 5, in which data are presented from two meters whose internal resistances were 150 and 450 ohms, respectively. Thus, the magnitude of the percentage correction varies both with the current produced and with the external resistance in the circuit.

Calibration of Photometer

A sample of pure synthetic riboflavin was obtained for calibrating the photometer. The absorption curve of this material is given in Figure 6. Its molecular extinction coefficient,  $2.78 \times 10^4$  at 4450 Å., was found to be in essential

TABLE I. DENSITY OF SOLUTIONS OF SYNTHETIC RIBOFLAVIN

Concentration Micrograms/ml.	Log $I_0/I$ Found	Log $I_0/I$ Calculated	Per Cent Deviation
21.12	0.569	0.682	-16.6
16.90	0.460	0.543	-15.3
16.51	0.448	0.531	-15.6
13.52	0.373	0.437	-14.7
12.38	0.340	0.399	-14.8
10.82	0.298	0.351	-15.1
8.25	0.225	0.267	-15.7
6.49	0.178	0.209	-14.8
4.13	0.111	0.132	-15.9
3.89	0.106	0.126	-15.9

Av. -15.4

agreement with that obtained by Kuhn (5). Since the response of the photometer depends not only upon the transmission of the filters but also upon the sensitivity of the photocell to different wave lengths and the energy distribution from the tungsten filament of the light bulb, the combined effect of these three factors has also been plotted in Figure 6. It is apparent that the final sensitivity of the instrument from 4000 to 5000 Å. is very nearly identical with the absorption curve of riboflavin.

In order to determine to what extent these filters would approximate the results obtained with monochromatic light, a sample of synthetic riboflavin was weighed on a microbalance and dissolved in distilled water. A series of dilutions was made up from this stock solution and the absorption of each solution was determined in the photometer. These results are given in Table I and demonstrate that the density ( $\log I_0/I$ ), as determined with the photometer, is 15 per cent less than the theoretical value obtained with monochromatic light. The fact that solutions of riboflavin follow Beer's law is illustrated in Figure 7, in which these density values have been plotted against concentration.

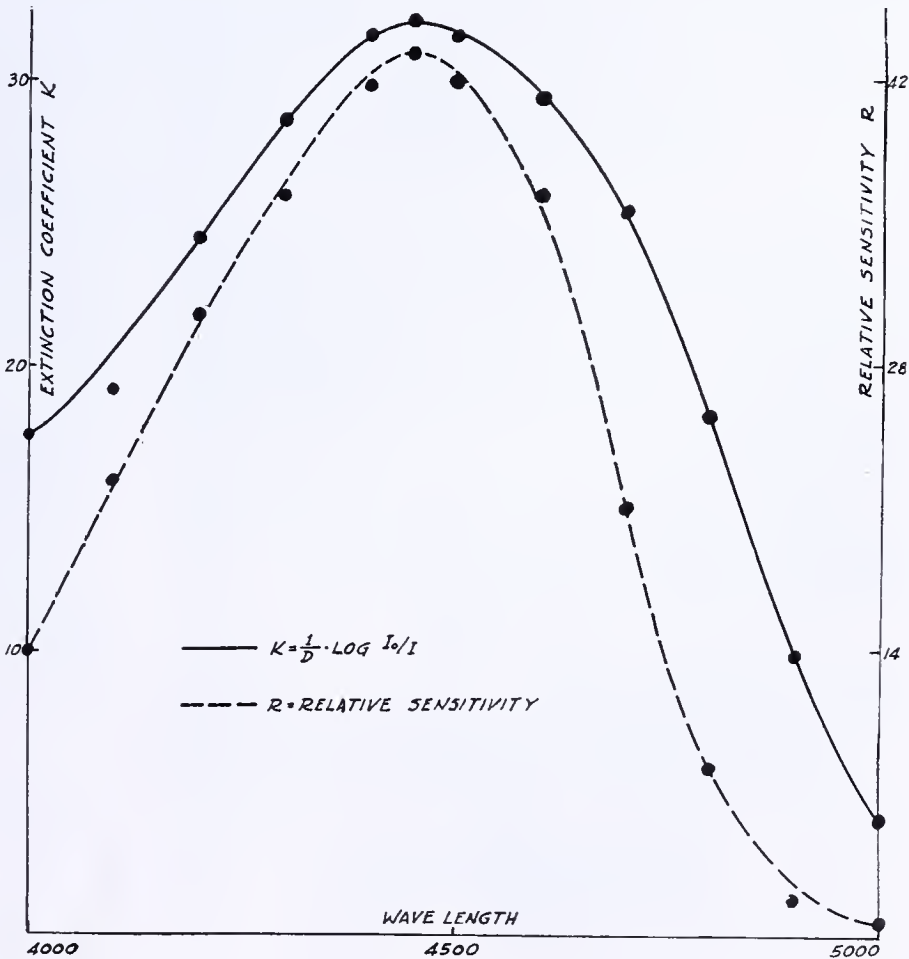


FIGURE 6. COMPARISON OF ABSORPTION CURVE WITH PHOTOMETER SENSITIVITY



For the purpose of reducing riboflavin to the leuco form, a solution is prepared by adding 5 per cent of sodium hyposulfite to a 2 per cent solution of sodium bicarbonate. This solution should be made up fresh each day and held in an ice bath while in use. One or two drops of this solution will reduce 20 ml. of a moderately concentrated solution of riboflavin. Riboflavin solutions of varying concentrations were reduced by this method, with the results shown in Table II.

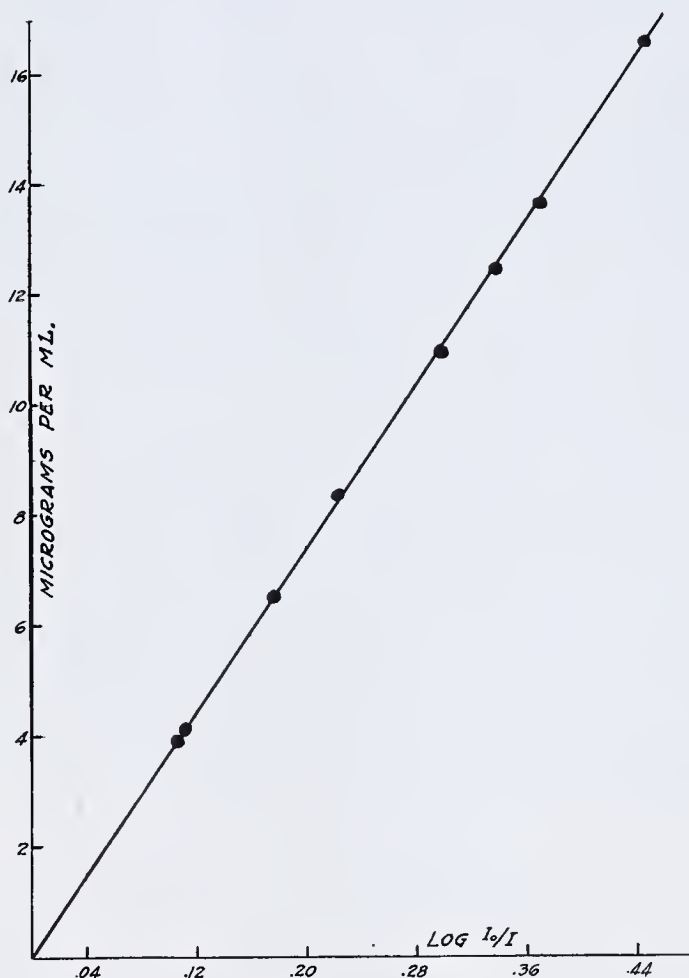


FIGURE 7. CALIBRATION CURVE

The residual light absorption indicates that at equilibrium only 90 per cent of the riboflavin is reduced. Consequently, the final values for the various concentrations of riboflavin, as determined by the photometer, must be multiplied by a factor 1.307. The deviation of the light absorption from that obtained with monochromatic light and the equilibrium concentration of reduced riboflavin have been included in this correction factor.

To illustrate the method of calculating the concentration from the readings of the photometer, it is necessary to start with the equation for the molecular extinction coefficient

$$K = \frac{2.3}{C \times D} \log I_0/I$$

in which  $C$  = concentration in moles per liter and  $D$  = thickness of absorbing layer in centimeters.

It has been found more convenient to express the concentration in micrograms per milliliter,  $c$ . Since a thickness of 1 cm. is always used and  $K$  equals  $2.78 \times 10^4$ , the above expression may be written

$$c = \frac{2.3 \times 376 \times 10^3}{2.78 \times 10^4 \times 1} \log I_0/I$$

or

$$c = 31.1 \log I_0/I$$

Two values of  $c$  are obtained for each solution and the difference between these two multiplied by the factor 1.307 gives the concentration of riboflavin in micrograms per milliliter,  $M$ .

$$M = 1.307 (c_1 - c_2)$$

If  $I_0$  is maintained constant, a table may be prepared relating  $I$  to  $c$ , so that for each reading of the microammeter the corresponding concentration in micrograms per milliliter will be given.

### Preparation of Extracts

Several solvents may be used for preparing extracts from dried milk products, but a 75 per cent solution of acetone in water has proved most satisfactory from the point of view of rapidity of extraction and purity of the extract. Varying amounts of sulfuric acid were added to the acetone-water mixture to determine the effect of acidity upon completeness of extraction. Table III shows the average of two determinations for each concentration of acid used.

It appeared that some acid was necessary for complete extraction, even though the amount of impurities was also increased.

The above solutions were neutralized before reading in the photometer. It had previously been found that pH had little, if any, effect upon the completeness of reduction, but a slight variation in the light absorption had been observed. Aqueous solutions of synthetic riboflavin were prepared and adjusted to various pH values by the addition of buffer solutions. All these solutions contained exactly the same amount of riboflavin and the pH was checked with a glass electrode. Several observations were made of the light absorption at each pH value. It was found that the maximum absorption occurred at pH 7.0. Each observation was calculated in per cent of this maximum reading and recorded in Table IV.

TABLE II. REDUCTION OF SOLUTIONS OF SYNTHETIC RIBOFLAVIN WITH SODIUM HYPOSULFITE

(Concentrations calculated in micrograms per ml.)		
Original Reading	After Reduction	Per Cent Unreduced
13.92	1.32	9.5
10.59	1.03	9.7
10.59	1.08	10.2
7.05	0.69	9.8
6.98	0.74	10.6
3.53	0.32	9.1
3.53	0.36	10.2
3.53	0.36	10.2
		Av. 9.8

TABLE III. EFFECT OF ACIDITY UPON COMPLETENESS OF EXTRACTION FROM DRIED MILK POWDERS

(Concentrations in micrograms per ml.)		
Normality of Acid	Riboflavin	Impurities Calculated as Riboflavin
0.00	2.09	0.63
0.05	2.11	0.50
0.10	2.27	0.69
0.15	2.22	0.82
0.20	2.49	0.78
0.25	2.28	0.83

TABLE IV. EFFECT OF pH ON LIGHT ABSORPTION OF SOLUTIONS OF SYNTHETIC RIBOFLAVIN

pH	Per Cent of Maximum Absorption
1.0	96.0
2.0	98.7
3.0	96.4
4.0	96.8
5.0	96.5
6.0	98.4
7.0	100.0
8.0	97.5
9.0	95.3
10.0	94.5



TABLE V. ACCURACY OF MEASURING SYNTHETIC RIBOFLAVIN  
(Concentrations in micrograms per ml.)

Actual Concentration of Riboflavin	Calculated Concentration of Riboflavin	Deviation
16.52	16.47	-0.04
12.39	12.49	+0.10
12.39	12.43	+0.04
8.26	8.31	+0.05
8.26	8.16	-0.10
4.13	4.20	+0.07
4.13	4.14	+0.01
4.13	4.14	+0.01
		Av. $\pm 0.05$

TABLE VI. REPRODUCIBILITY OF MEASUREMENT OF RIBOFLAVIN  
IN DRIED MILK PRODUCTS  
(Concentrations in micrograms per gram)

Sample	Number of Observations	Mean	Probable Error of Single Observation
1	12	29.8	$\pm 0.87$
2	10	21.4	$\pm 0.62$

After neutralizing the extracts, it is necessary to filter off the residual milk powder. Considerable difficulty was experienced in washing these precipitates free from riboflavin. With a known volume of solvent, it should be possible to use the filtrate without washing the precipitate or making the filtrate up to volume, provided that riboflavin is not preferentially adsorbed by the precipitate. In order to test this hypothesis, two 10-gram samples of dried whey were taken, a known amount of pure riboflavin was added to one sample, and both samples were then extracted, neutralized, and filtered. The light absorption of the filtrates was determined without washing the precipitates or making the filtrates up to volume.

Riboflavin Added Micrograms	Riboflavin Found Micrograms
0	300
160	460

Based upon these experiments, the following method of extracting riboflavin from dried milk products was devised.

An acid-acetone solution is prepared by making 750 ml. of acetone up to 1 liter with *N* sulfuric acid. A 15-gram sample of milk powder is weighed into a 250-ml. Erlenmeyer flask and 100 ml. of the acid-acetone solution are added. It has been found that certain impurities are readily destroyed by the addition of hydrogen peroxide. Therefore, depending upon the degree of caramelization exhibited by the sample, from 1 to 3 ml. of 30 per cent hydrogen peroxide are added to the sample. The flask is connected to a reflux condenser, and the solution is boiled for 20 minutes, although complete extraction is generally obtained by 15 minutes of refluxing. The flask is allowed to cool while still connected to the condenser to prevent loss of solvent. It is then tightly stoppered with a paraffined cork and placed in the refrigerator for 30 minutes. The flask is then removed and the solution neutralized by the addition of 25 ml. of *N* sodium hydroxide. Depending upon the amount of hydrogen peroxide used, from 22 to 24 ml. of a buffer solution are added, which makes a total of 150 ml. of solvent for a 15-gram sample. For dried whey, a buffer solution of pH 6.8 is used. For dried skim milk and dried buttermilk a buffer solution of pH 4.6 is used. The flask is returned to the refrigerator for 30 minutes, after which the solution may be filtered. The filtrate represents a 10 per cent solution of the sample and may now be read in the photometer. The amount of sodium hypofluorite required to reduce this solution will vary with the completeness with which the hydrogen peroxide has been decomposed. Usually from 15 to 30 drops will be required, and a correction may be made for the increase in volume of extract caused by this addition.

In order to demonstrate the accuracy with which pure riboflavin may be measured in the photometer, reference will be made to the data presented in Table II regarding solutions of

synthetic riboflavin of known concentration. Table V presents the actual concentrations, as well as the concentrations calculated from the photometric reading by means of the correction factor. The reproducibility with which riboflavin may be extracted from dried milk products and measured in the photometer is illustrated in Table VI, based upon observations of two dried milk products. The probable error of a single observation is less than 1 microgram per gram.

Discussion

The manufacturers of blocking-layer photocells frequently state that no external potential should be applied to these instruments. However, this invariably results when a photocell is connected directly to a meter. The use of the zero-potential circuit enables one to use the cell at all times in the manner in which it was intended to be used. It might have appeared possible to dispense with any correction had the magnitude of the correction been a constant percentage of the correct reading, since in absorption spectrophotometry only the ratios of two readings are used. However, the correction is not a constant factor and other considerations influence the choice of circuit. The use of the zero-potential circuit greatly reduces the variability which is ordinarily found between photocells of the same manufacturer. This is true because the greatest source of variation between cells lies in the internal leakage resistance, which no longer influences the readings when the electrodes are maintained at zero potential. Also, changes in the internal leakage resistance due to differences in atmospheric conditions will no longer influence the readings. Consequently, identical readings are obtained by operators in widely separated laboratories.

By the proper selection of filters, the photometer may be used for many types of colorimetric measurements. One of the limitations in the use of filters instead of a monochromator is that strict proportionality between concentration and density ( $\log I_0/I$ ) is obtained only over a limited range of concentrations, if the transmission curve of the filter does not exactly coincide with the absorption band of the pigment (8). Consequently, if the photometer itself does not give a linear response to varying light intensities, a calibration curve must be plotted for each pigment. The curvature of this line will be made up of two components: (1) inherent in the photometer itself, and (2) due to a failure of the filters.

With the present instrument it is only necessary to determine over what range the filters fit the absorption curve of the unknown in order to make direct calculation of the concentration from the readings of the photometer. This becomes important when it is necessary to determine one component of a mixture of pigments by the difference between two readings. This may be done when it is possible to destroy or decolorize the pigment being measured. It is obvious that an error will be involved if such a pair of readings is applied to a curved calibration curve, since the error due to the filters depends only upon the concentration of the pigment being measured. However, if the photometer is constructed to give a linear response to varying light intensities and the concentration of the unknown pigment is within the limits set by the filters, the change in light absorption upon removing the pigment will be a linear function of the concentration of the pigment.

The method of determining riboflavin which has been presented in this paper will give accurate and reproducible results when applied to well prepared samples of dried milk products, but when the milk powders have been caramelized, or when other feedstuffs are present in the sample, it is necessary to subject the extracts to further purification.



In several cases the method has been applied to milk products which were also assayed for riboflavin by means of chicks. The chick assays upon six samples gave an average value of 21.2 micrograms per gram. An average value of 21.5 micrograms per gram was obtained by the photometric test. The method presented in this paper is preferred because of its rapidity, and because biological assays may be complicated at times by the presence or absence of nutritional factors which are not as yet clearly defined.

The absolute accuracy of this method depends upon the purity of the sample of synthetic riboflavin used as a standard. Several samples of crystalline riboflavin were obtained from different sources at the time of standardizing the method and none of these appeared to be quite so pure as the sample used. This conclusion was based both upon the light absorption and the completeness of reduction. Since that time an occasional sample has been encountered which appeared to be reduced to a greater extent than the standard. When a satisfactory standard of reference has been obtained it may be necessary to alter slightly the above correction factor for calculating the concentration of riboflavin.

When other instruments are set up according to the above directions the same correction factor may be used for calculating riboflavin concentration. Some care must be taken to assure that exactly 90 per cent reduction of the riboflavin is obtained. Variation in the completeness of reduction may occur through incomplete removal of the peroxide or decomposition of the hyposulfite solution.

### Conclusions

A photometer has been described which utilizes a zero-potential circuit in connection with a blocking-layer photocell. Such an instrument gives a linear response to varying light intensities, and offers advantages in regard to proper use of the photocell, reproducibility of results, and application to certain spectrophotometric measurements.

Riboflavin may be extracted from dried milk products by refluxing with a dilute solution of acid in 75 per cent acetone.

Certain unstable colored impurities may be destroyed by including from 1 to 3 per cent of hydrogen peroxide in the solvent. The resulting solution, after neutralizing and filtering, may be used for quantitative measurements since riboflavin is not preferentially adsorbed by the precipitated milk solids. By reduction with sodium hyposulfite, 90 per cent of the color of riboflavin is removed. Observation of the light absorption before and after reduction enables one to calculate the concentration of the solution to  $\pm 0.05$  microgram per ml.

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## Boron Determination in Soils and Plants

### Using the Quinalizarin Reaction

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IN HUMID regions, boron often exists in soils largely as tourmaline, a boroaluminum silicate which is not readily available. The available boron, probably existing often largely as the calcium salt, is usually present in humid regions in amounts of less than one part per million. In plant tissue, boron is often present to the extent of 25 parts per million, and since it is now recognized as an essential plant nutrient, its determination in both soils and plants assumes considerable importance. Methods used in the past for making these determinations have not been very satisfactory in some respects, and the present paper reports the results of an attempt at improvement.

In the past, the turmeric paper test described by Bertrand and Agulhon (1) has often been used in the determination of small amounts of boron. As the turmeric paper is not very sensitive to small differences in amounts of boron, and difficulties are encountered in making accurate comparisons with the standard, the method leaves much to be desired. The spectroscopic method has recently been used by a number of

investigators (3, 6) to determine the boron content of plant materials. It seems to give fairly good results, but requires rather elaborate equipment and is time-consuming. The titrimetric procedure, involving the use of polyhydroxy alcohols and discussed in detail by several workers (8, 11), is not well adapted for the rapid determination of the small amounts sometimes encountered in soil and plant analysis, because the method involves distillation which is time-consuming, and because traces of buffering substances which are difficult to remove may seriously interfere with the results.

### Quinalizarin Reaction

It has been known for a considerable number of years that the addition of boric acid to many of the hydroxyanthraquinones in concentrated sulfuric acid will cause a marked color change which may be used for the identification of these quinones. Recently this color change was applied to the determination of boron. For this purpose, Feigl and Krumholz (5) tried purpurin, alizarin S, and quinalizarin. Quinaliz-



arin (1,2,5,8-tetrahydroxyanthroquinone) was found to be the most sensitive, changing from a pink color to a bluish hue with increasing concentrations of boron. Scharrer and Gottschall (8) found quinalizarin to be better than purpurin. These investigators found that fluorides, nitrates, dichromates, and other oxidizing compounds interfere in the test by turning the solution colorless.

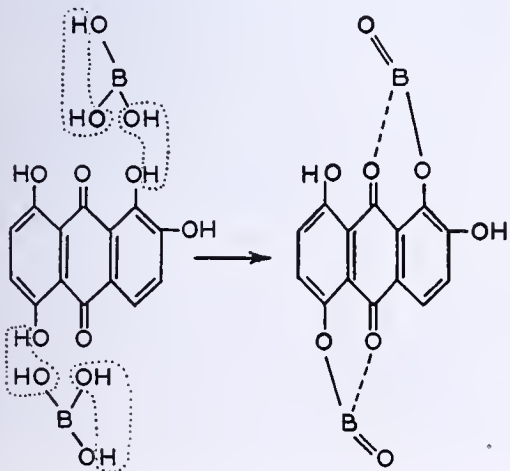
The authors found that if there are over 500 parts per million of water-soluble fluorides in soils, or 5000 parts per million of total fluorides in soils or plant tissue, the color on which the procedures to be described depend will be partially destroyed. Because of the insolubility of calcium fluoride, the presence of appreciable amounts of water-soluble fluorides in soils is rare. The small amounts ordinarily present in soils and plants do not interfere. Larger amounts will destroy it entirely. When necessary, fluorides are removed easily by precipitation with thorium chloride and subsequent filtration.

The only oxidizing substance found in soils and plants that interferes in the quinalizarin reaction is nitrate. In the procedures to be described, this is removed by ignition.

The only known substance (7, 10) that is similar to boron in causing a color change with quinalizarin is germanic acid. Poluektov (7) found that this also forms complex acids with polyhydroxy alcohols and thus enters into an alkalimetric titration like boric acid. In tests made by the authors, it was found that it takes over 200 times as much germanium as boron to produce a certain color change in the quinalizarin reaction. This means that in the procedures described below there would have to be over 20 parts per million of water-soluble germanium in soils, and over 200 parts per million of total germanium in soils or plant tissue, to produce a visible color change. Since the occurrence of germanium in soils and plants is rare, and since it takes considerable amounts of germanium to produce a visible color change, interference by germanium in the quinalizarin test for boron in soils and plants appears to be remote.

An all-important factor in the determination of boron by means of the quinalizarin reaction is the concentration of sulfuric acid in which the color is developed. Smith (9) found that at least 44 per cent by weight of sulfuric acid must be present in the solution in order to produce a visible color change due to boron. He found that the sensitivity or color change increases as the concentration of sulfuric acid increases until about 93 per cent of acid by weight is present; beyond this the sensitivity decreases. Smith indicates that the method is sensitive to 0.001 mg. of boric acid. He applied the method to the determination of boron in alloys.

The interaction of boric acid with quinalizarin is undoubtedly very similar to its reaction with dihydroxyanthraquinones, which form chelated compounds with boric acid as shown by Feigl and Krumholz (5). In accordance with this, the quinalizarin reaction with boric acid takes place:



Four molecules of water are split off and a chelated ring forms as indicated. A similar reaction takes place between boric acid and open-chain polyhydroxy alcohols (4). The reaction given reflects the necessity of the presence of concentrated sulfuric acid to aid in splitting off the water and prevent the reaction from reversing.

For the determination of easily soluble boron in soils, the writers first tried the turmeric paper test but the results obtained were not entirely satisfactory. The quinalizarin color reaction was then applied to both soil and plant analysis, and a satisfactory procedure was developed, the details of which follow.

### Application of Quinalizarin Reaction

In the application of the quinalizarin reaction, it was found that a concentration of about 93 per cent by weight of sulfuric acid in the final test solution, obtained by adding 98.5 per cent acid by weight, gives the most satisfactory results for small amounts. With this concentration and method of comparison used, it was possible to distinguish 0.0001 mg. of boron from a blank test.

Nitrates in amounts usually found in soil solutions may be reduced and removed by adding potassium carbonate and powdered aluminum to the soil extract and evaporating. Later it was found that evaporation and gentle ignition in the presence of potassium carbonate or calcium hydroxide were more convenient and fully effective in removing the nitrates ordinarily found in soil extracts. This also destroys organic matter which otherwise produces a brown color and interferes with the test color.

Organic matter and many other substances may also be separated by distilling the boron as the methyl ester of boric acid. To do this, the soil extract is evaporated to dryness and then taken up in 85 per cent phosphoric acid and some absolute methyl alcohol. The solution is placed in a distilling flask (boron-free glass) and the methyl borate distilled into an aqueous solution of potassium carbonate. The presence of a small amount of free water prevents the complete distillation of the boron. This may be guarded against by the addition of a small amount of phosphoric anhydride.

The distillation and subsequent evaporation necessary to obtain the desired concentration were time-consuming and laborious; hence, the simple ignition procedure was adopted to destroy both nitrates and organic matter, which appear to be the only interfering substances ordinarily present in soil extracts. When 0.1 gram of potassium carbonate was added to the soil extract, and the extract was then evaporated to dryness and gently ignited, there was no loss of boron, while nitrates and organic matter were destroyed. Platinum containers must be used when the ignition is made with potassium carbonate, since this reagent attacks both quartz and porcelain ware. Calcium hydroxide may be used in place of potassium carbonate, making possible evaporation and ignition in porcelain or quartz dishes. The ignition and distillation procedures gave identical results when applied to synthetic solutions and soil extracts.

Standard color solutions for the colorimetric comparisons may be prepared by adding the appropriate amounts of the reagents to varying amounts of boron as in testing unknown solutions. These standards are permanent if kept in stoppered comparison tubes, so as to prevent absorption of water. Since it is necessary to remove the stoppers to make comparisons most advantageously, absorption of water cannot be entirely prevented; hence, these standards usually deteriorate in the course of a week or so, depending upon amount of exposure. The color comparisons can, of course, also be made by means of a photoelectric colorimeter.



TABLE I. PREPARATION OF COLOR STANDARDS

No.	Boron Present in Color Standards Mg.	Amounts Required to Produce Corresponding Standards	
		Distilled water Cc.	Boron stock solutions B and C Cc.
1	0.0000	1.00	0.00
2	0.0002	0.80	0.20 (C)
3	0.0004	0.60	0.40 (C)
4	0.0006	0.40	0.60 (C)
5	0.0008	0.20	0.80 (C)
6	0.0010	0.00	1.00 (C)
7	0.0015	0.85	0.15 (B)
8	0.0020	0.80	0.20 (B)
9	0.0025	0.75	0.25 (B)
10	0.0030	0.70	0.30 (B)
11	0.0035	0.65	0.35 (B)
12	0.0040	0.60	0.40 (B)

### Preparation of Reagents

**SULFURIC ACID, 98.5 PER CENT BY WEIGHT.** Although the strength of sulfuric acid may vary from 98 to 99 per cent by weight, for small amounts of boron it is very important to keep it within these limits, and this requires accurate work in its preparation and great care in its use and storage. The acid is prepared by mixing ordinary concentrated sulfuric acid with fuming sulfuric acid. To facilitate the calculations involved in determining the proportion of each to be mixed, strengths are best expressed in terms of sulfur trioxide rather than sulfuric acid. Accordingly, the desired 98.5 per cent sulfuric acid becomes 80.4 per cent sulfur trioxide. The proportion of each to be mixed varies, of course, with the strengths of the acids. The concentrated acid usually contains about 95 per cent of sulfuric acid by weight, and the fuming 20 to 30 per cent of free sulfur trioxide. The exact strength in each case is determined by weighing out 2 grams or more of the acid in a 25-cc. weighing bottle, and after diluting, titrating with 1.0 *N* sodium hydroxide. In the case of the concentrated sulfuric acid, the weighing bottle with contents is placed in a beaker of water, and, after mixing, the acid is titrated. In the case of the fuming acid, the weighing bottle containing the acid is dropped into a second 100-cc. weighing bottle containing about 30 cc. of water. As the bottle is dropped, the cover of the 25-cc. bottle is removed, and then the cover of the larger bottle is quickly replaced. After standing overnight or until fuming has entirely ceased, the two weighing bottles with covers removed are placed in a liter beaker containing 300 to 400 cc. of water. It is advisable to place the cover of the larger bottle in the beaker also, to prevent any loss of acid which might be on the cover. After mixing, the acid is titrated. The strengths in terms of sulfur trioxide are then calculated by means of the following formula:

$$\frac{\text{cc. NaOH titration} \times \text{normality} \times 0.04003}{\text{weight of concentrated or fuming H}_2\text{SO}_4} \times 100 = \text{percentage by weight of SO}_3 \text{ in each case}$$

After the strengths of the acids have been determined in terms of sulfur trioxide, the proportion of each to be mixed to make 100 grams of 98.5 per cent sulfuric acid, which contains 80.40 per cent of sulfur trioxide, is calculated as follows:

$$\begin{aligned} \text{Let } x &= \text{grams of concentrated sulfuric acid needed} \\ 100 - x &= \text{grams of fuming sulfuric acid needed} \\ \text{Let } a &= \text{strength of concentrated sulfuric acid in terms of sulfur trioxide} \\ &\text{expressed decimally} \\ b &= \text{strength of fuming sulfuric acid in terms of sulfur trioxide expressed} \\ &\text{decimally} \\ \text{Then, } ax + b(100 - x) &= 80.40, \text{ and } x \text{ is solved for} \\ \text{EXAMPLE. Strength of concentrated sulfuric acid found by titration was} \\ 77.78 \text{ per cent sulfur trioxide. Strength of fuming sulfuric acid found by} \\ \text{titration was 87.41 per cent sulfur trioxide. Substituting these values in the} \\ \text{formula above and solving for } x, \text{ there is obtained:} \\ 0.7778x + 0.8741(100 - x) &= 80.40 \\ 0.0963x &= 7.01 \\ x &= 72.79 \text{ grams, amount of concentrated} \\ &\text{acid needed} \\ 100 - 72.79 &= 27.21 \text{ grams of fuming acid needed in} \\ &\text{making 100 grams of desired} \\ &\text{mixture containing 98.5 per cent} \\ &\text{H}_2\text{SO}_4 \end{aligned}$$

**QUINALIZARIN SOLUTION.** Dissolve 0.01 gram of quinalizarin in 100 cc. of strong sulfuric acid made by diluting 9 volumes of 98.5 per cent by weight sulfuric acid with one volume of water. Store in a glass-stoppered bottle.

**SULFURIC ACID, APPROXIMATELY 0.36 *N*.** Dilute 5 cc. of 95 to 96 per cent by weight sulfuric acid to 500 cc. with distilled water.

**SULFURIC ACID, APPROXIMATELY 4 *N*.** Dilute 50 cc. of 95 to 96 per cent by weight sulfuric acid to 450 cc. with distilled water.

**CALCIUM HYDROXIDE, SATURATED SOLUTION.** Add 5 to 10 grams of calcium hydroxide to 500 cc. of distilled water. Shake well and allow to settle.

**POTASSIUM CARBONATE SOLUTION.** Dissolve 40 grams of anhydrous potassium carbonate in 100 cc. of distilled water. Five drops of this contain about 0.1 gram of potassium carbonate.

### Preparation of Color Standards

Dissolve 2.8578 grams of boric acid in 1000 cc. of distilled water. This solution contains 0.5 mg. of boron per cc. and serves as the primary (A) base stock solution. Prepare a second (B) stock solution containing 0.01 mg. of boron per cc. by diluting 20 cc. of the primary base stock solution to 1000 cc. with distilled water, and a third (C) stock solution containing 0.001 mg. of boron per cc. by diluting 100 cc. of the second stock solution to 1000 cc.

Transfer varying amounts of the second stock solution for amounts above 0.001 mg. of boron, and of the third stock solution for the others, to boron-free test tubes or glass vials. Glass vials approximately 20 × 100 mm. are convenient and satisfactory for this purpose, and the amounts of boron given in Table I produce a satisfactory range of colors. In order to have the correct concentration of acid when the color is developed, it is necessary to have exactly 1 cc. of boric acid solution in each vial. This is conveniently done by dispensing the boron stock solutions from burets, and then adding water from another buret to bring the volume to 1 cc. in each case. Now, add 9 cc. of the 98.5 per cent sulfuric acid, or other acid, to be used with the unknown test solutions. Stopper the vials, cool, and add 0.5 cc. of the quinalizarin solution. After 15 minutes or more the color becomes fully developed and the standards are ready for use. These colors are permanent if the vials are kept stoppered to prevent absorption of water.

### Determination of Available Boron in Soils

Most of the available boron in soils is undoubtedly water-soluble. It was found that when a known amount of soluble boron in the form of boric acid was added to several soils free of water-soluble boron, and the soils were then dried, the added boron could be completely recovered by adding water, boiling for 5 minutes, and then filtering. The addition of hot water, followed by shaking for 30 minutes and then filtering, did not result in complete recovery. Complete recovery may be effected by extraction with dilute acid. This procedure, however, raises complications when calcareous soils are encountered, because of the difficulty of regulating the acidity. Furthermore, tests made with acid extractions of calcareous soils indicated that the results thus obtained often do not correlate well with crop indications of the boron status. After numerous tests, refluxing of the soil-water suspension for 5 minutes appeared to be the best procedure. More boron was extracted by refluxing from 5 to 10 minutes than either for shorter or longer periods. Boiling with a reflux condenser, the volume remains constant, and thus an aliquot is later more easily taken. The details of the analytical procedure finally adopted follow.

**ANALYTICAL PROCEDURE.** Place a 20-gram sample of the soil (air-dried and 20-meshed) in a 125-cc. Florence flask (boron-free glass), add 40 cc. of distilled water, and then attach a reflux condenser. Boil for 5 minutes, disconnect the condenser, stopper the flask, cool contents, and filter with suction on a Büchner funnel or centrifuge until the supernatant liquid is clear. Clarification may be facilitated by working with a warm solution or adding not more than 0.05 gram calcium chloride dihydrate. Place a 20-cc. aliquot of the clear extract in a platinum dish and add 5 drops of the potassium carbonate solution, or in a porcelain crucible and add 2 cc. of a saturated solution of calcium hydroxide. Evaporate to dryness and ignite gently to destroy nitrates and all organic matter. After cooling, add 5 cc. of approximately 0.36 *N* sulfuric acid, and triturate thoroughly with a policeman.



TABLE II. AVAILABLE OR WATER-SOLUBLE BORON FOUND IN FIELD TEST PLATS FERTILIZED WITH BORAX

Source of Sample	Type of Soil	pH	Boron Applied as Borax	Available Boron Found in Soils		
				A	B	Av.
				<i>P. p. m.</i>		
Plat 10	Clyde silt loam	8.0	0.00	0.50	0.50	0.50
Plat 11	Clyde silt loam	7.8	0.55	1.00	1.00	1.00
Plat 12	Clyde silt loam	7.6	1.10	1.00	1.10	1.05
Plat 13	Clyde silt loam	7.5	1.65	1.30	1.30	1.30
Plat 14	Clyde silt loam	7.4	2.20	2.60	2.50	2.55
Plat 15	Clyde silt loam	7.8	2.75	2.30	2.20	2.25
Plat 100	Clyde sandy loam	8.0	0.00	0.40	0.45	0.43
Plat 101	Clyde sandy loam	8.0	1.10	0.90	0.95	0.93
Plat 23	Poygan clay loam	6.3	0.00	0.45	0.47	0.46
Plat 24	Poygan clay loam	6.4	1.10	1.50	1.40	1.45

TABLE III. BORON FOUND IN SOILS TO WHICH KNOWN AMOUNTS OF BORON AS BORIC ACID HAD BEEN ADDED

Type of Soil	Boron Added	Total Boron Found			
		A	B	C	Av.
		<i>P. p. m.</i>			
Plainfield sand	0	2.0	2.0	2.0	2.0
	10	12.0	12.0	12.0	12.0
	20	22.0	22.0	22.0	22.0
Poygan clay loam	0	20.0	20.0	20.0	20.0
	10	28.0	30.0	30.0	29.3
	20	40.0	40.0	38.0	39.3
Miami silt loam	0	28.0	28.0	29.0	28.3
	10	38.0	38.0	38.0	38.0
	20	46.0	48.0	48.0	47.3

Place a 1-cc. aliquot of this solution in a comparison vial (20 X 100 mm.), add 9 cc. of the 98.5 per cent sulfuric acid, stopper the vial, and cool. After cooling, add 0.5 cc. of the quinalizarin reagent to the test solution and mix thoroughly by gently whirling the vial. Allow to stand for at least 15 minutes, and then determine the boron content by comparing with a set of standards. The final comparison is best made by removing the stopper from the standard and making a vertical observation against a white background, as is usually done in colorimetric comparisons.

**TYPICAL RESULTS.** Table II gives the amounts of available boron found in a number of field plats variously fertilized with borax. The borax was applied several months in advance of the soil sampling, and hence, some losses due to leaching undoubtedly occurred, which probably explains in part the incomplete recovery of the added boron. Some of the boron may also have become fixed in unavailable form. With these limitations in mind, the correlation between amounts of boron added and found appears satisfactory. Additional results, recently obtained and to be published elsewhere, correlate well with the crop indications.

Determination of Total Boron in Soils

In determining the total boron content of soils by means of the fusion method, it is necessary to use a high proportion of sodium carbonate to soil. Treatment of the melt obtained with water alone will bring all the boron into solution, but is inconvenient, being slow and requiring much water. Addition of sulfuric acid to the water, so that the final reaction of the solution falls within the pH range of 5.5 to 6, hastens the disintegration of the melt and leaves most of the sesquioxides and silica in insoluble form. Addition of alcohol up to 60 to 70 per cent by volume at this point serves to throw down most of the large amount of sodium sulfate which has been formed. This leaves all the boron and only a small amount of salts in solution. After the final evaporation, it is necessary to ignite because of the small amount of nonvolatile organic matter usually introduced with the alcohol.

**ANALYTICAL PROCEDURE.** Fuse 0.5 gram of soil with 3 grams of anhydrous sodium carbonate in a platinum crucible. Cool and place the crucible in a 250-cc. beaker containing about 50 cc. of distilled water. Place a cover glass on the beaker and add approximately 4 N sulfuric acid from time to time until the melt has disintegrated and the solution has a reaction in the range of pH 5.5 to 6.0. Transfer the resulting solution to a 500-cc. volumetric flask. Wash the beaker and crucible several times with distilled water and add the washings to the flask. The total volume of solution should now not exceed 150 cc. Add methyl or ethyl alcohol to the flask until a volume of 500 cc. is reached and mix the contents thoroughly. Filter the solution or centrifuge until the supernatant liquid is clear.

Place a 400-cc. aliquot of the clear solution in a 500-cc. beaker (boron-free glass) and add 100 to 150 cc. of distilled water to prevent subsequent precipitation. Add potassium carbonate until the solution is alkaline, evaporate to a small volume, and transfer to a platinum dish. Evaporate to dryness and ignite to destroy organic matter. After cooling, add 4 cc. of approximately 0.36 N sulfuric acid, and triturate thoroughly with a policeman. Place a 1-cc. aliquot of this solution in a comparison vial, add 9 cc. of the 98.5 per cent sulfuric acid, stopper the vial, and cool. After cooling, add 0.5 cc. of the quinalizarin reagent to the test solution and mix thoroughly by gently whirling the vial. Allow to stand at least 15 minutes before comparing with standards.

**RESULTS.** Table III gives results obtained in the analysis of several soils with this procedure. To some samples of these soils known amounts of boron had been added; recovery of the added boron was satisfactory. A Bureau of Standards sample of glass containing 0.22 per cent of boron was analyzed with the procedure just described, and six determinations gave 0.21, 0.23, 0.225, 0.22, 0.20, and 0.225 per cent of boron. The quinalizarin colorimetric procedure, because of its extreme sensitivity, is thus well adapted for the determination of the small amounts of boron usually found in soils, plants, and many other substances. When materials containing several per cent of boron are analyzed, the sample involved in the final comparison is so small that any slight error at this stage becomes multiplied many times in the calculations that follow. The titrimetric procedure may thus be better adapted to analyses involving high contents of boron. It is possible that a better adaptation of the colorimetric procedure for high contents might be attained by lowering the acidity of the test solution so as to require a larger amount of boron to effect a certain change in color intensity. The color standards whether for direct comparison or photoelectric calibration would, of course, need to be developed with the lower acidity also.

TABLE IV. BORON FOUND IN PLANT TISSUE ASHED WITH AND WITHOUT POTASSIUM CARBONATE

Nature of Plant Tissue	Nature of Culture	(Oven-dry basis)					
		Amounts of Boron					
		Ashed without K <sub>2</sub> CO <sub>3</sub>			Ashed with K <sub>2</sub> CO <sub>3</sub>		
		A	B	Av.	A	B	Av.
<i>P. p. m.</i>							
Alfalfa, leaves and stems	Quartz pot culture	36.0	36.0	36.0	35.0	34.0	34.5
Lettuce, leaves	Quartz pot culture	14.0	14.0	14.0	13.0	13.5	13.25
Beet, red, leaves and petioles	Field culture	30.0	30.0	30.0	28.0	30.0	29.0
Beet, red, leaves and petioles	Field culture	26.0	24.0	25.0	25.0	24.0	24.5
Beet, red, roots	Field culture	9.0	9.0	9.0	8.0	8.0	8.0
Red cabbage, leaves	Field culture	11.5	12.0	11.75	12.0	12.0	12.0
Okra, leaves	Field culture	26.0	26.0	26.0	26.0	24.0	25.0
Tomato, leaves and petioles	Field culture	40.0	38.0	39.0	40.0	40.0	40.0
Shortleaf pine seedlings	Field culture	9.0	9.0	9.0	9.0	9.0	9.0
Horsetail, leaves	Field culture	11.0	11.0	11.0	11.0	11.0	11.0
Cattail, leaves	Field culture	12.0	12.0	12.0	11.0	12.0	11.5
Lemon, fruit pulp	Field culture	11.5	11.5	11.5	11.5	11.5	11.5
Lemon, fruit juice <sup>a</sup>	Field culture	0.3	0.3	0.3	0.3	0.3	0.3

<sup>a</sup> Results calculated on basis of juice, not oven-dried residue.



TABLE V. BORON CONTENT OF VARIOUS PLANTS GROWN ON SAME SOIL

(Oven-dry basis)				
Species of Plant	Portion of Plant	Amounts of Boron Found		
		A	B	Av.
		<i>P. p. m.</i>		
Sweet corn	Leaves	4	4	4.0
Kale	Leaves and petioles	12	13	12.5
Leek	Leaves and bulb	12	13	12.5
Red cabbage	Leaves	12	12	12.0
Green beans	Leaves and stems	15	15	15.0
Carrot	Roots	15	14	14.5
Carrot	Leaves and petioles	16	18	17.0
White cabbage	Leaves	16	18	17.0
Okra	Leaves	18	18	18.0
Tomato	Leaves	40	39	39.5

### Determination of Total Boron in Plants

**ANALYTICAL PROCEDURE.** Place a 0.25- to 0.50-gram sample of plant tissue (oven-dried and ground) in a platinum crucible or porcelain evaporating dish and ignite gently to a white or gray ash. After cooling add 5 cc. of approximately 0.36 *N* sulfuric acid and triturate with a policeman. After settling, place a 1-cc. aliquot of the clear supernatant liquid in a comparison vial, add 9 cc. of the 98.5 per cent sulfuric acid, stopper the vial, and cool. Then add 0.5 cc. of quinalizarin solution, stopper, and mix well by whirling gently. Allow to stand at least 15 minutes and then determine the boron content by comparing with a set of standards.

**RESULTS.** The results of analyses with and without the addition of potassium carbonate prior to ashing, given in Table IV, show that it is not necessary to add a base to the plant tissue to prevent loss of boron on ashing. Several plants—namely, shortleaf pine, horsetail, and cattail—which have a preponderance of acidic constituents in their ash, were ignited with and without the addition of a base; no significant differences in boron content were noted. A sample of lemon juice was neutralized, and this juice, together with a sample to which no base had been added, was evaporated to dryness and ignited. The results show that even with this very acid juice the boron suffers no loss on ignition. Other workers (2, 6) have obtained similar results. Apparently practically all plant tissue and juices release sufficient bases from organic combination when ignition takes place to hold the boron as a nonvolatile borate.

Table V gives the boron content of a number of species of plants grown on the same soil. The amounts found correspond well with the amounts found by other investigators (2). The boron content of corn leaves is much lower than that of many vegetables. Vegetables, fruits, truck crops, and legumes seem to suffer sooner from a lack of boron than the grasses, and this seems to be correlated with the boron content of these plants.

Table VI gives the boron content of a number of species of plants and the available boron in the culture mediums in which the plants were grown. These data show that there is some correlation between the amount of available boron in the culture medium and that found in plant tissue grown thereon. This is especially true in the case of quartz cultures in which the amount of available boron can be closely controlled.

### Precautions

Since many c. p. chemicals contain appreciable amounts of boron, it is essential that all chemicals used in the determination of boron be tested for freedom from this element. Pyrex glass contains about 11 per cent of boric oxide and may cause serious contamination if used in this determination. Kavalier or other boron-free glassware should be used. All reagents should be stored in containers made of boron-free glass.

Common soft-glass bottles are usually satisfactory. Great care must be exercised in measuring the 1-cc. aliquot of the unknown to which are added the reagents for color development, because an error of 1 drop in this measurement may cause an error of from 5 to 10 per cent in the final result, through its influence on the final acid concentration in the mixture. The 98.5 per cent sulfuric acid reagent and the quinalizarin solution should be stored in bottles equipped with tightly fitting glass stoppers to prevent absorption of water, and these bottles should not be left unstoppered. The 98.5 per cent sulfuric acid solution should be tested from time to time, so as to be certain of its strength. Pipets, burets, and all other measuring instruments should be calibrated.

TABLE VI. BORON FOUND IN PLANT TISSUE PRODUCED UNDER VARIOUS CONDITIONS

(Oven-dry basis)			Amounts of Boron	
Species of Plant	Portion of Plant	Nature of Culture	Avail- able in culture medium	Total in plant tissue
— <i>P. p. m.</i> —				
Beets, red	Leaves and petioles	Field culture	0.43	14.5
	Roots	Field culture	0.43	6.0
	Leaves and petioles	Field culture	0.93	24.0
	Roots	Field culture	0.93	9.0
Lettuce	Leaves	Quartz pot culture	0.00	3.8
			0.25	7.0
			0.50	10.3
			1.00	13.5
			2.00	10.5
Alfalfa	Leaves and stems	Quartz pot culture	0.00	8.0
			0.50	33.5
			1.00	41.5
			2.00	51.0

### Summary

By means of the quinalizarin color reaction it is possible with proper control of the acidity to detect 0.0001 mg. of boron. This reaction was found to be well adapted for the detection and colorimetric determination of the small amounts of boron found in soils, plants, and many other materials. Interfering substances ordinarily present in soil extracts and plant tissues are easily removed by a simple ignition procedure.

The available boron of soils is extracted by refluxing with water for 5 minutes. An aliquot of the filtered extract is then made alkaline and evaporated to dryness. The residue is ignited to destroy organic matter and nitrates, and then taken up with dilute acid, after which the quinalizarin colorimetric test for boron is applied.

In the determination of total boron in soils and silicates, a sodium carbonate fusion is made and the resulting melt is dissolved at pH 5.5 to 6.0 so as to leave insoluble most of the silica and sesquioxides. The bulk of the sulfate is thrown out of solution by the addition of alcohol. The filtered solution is made alkaline, evaporated to dryness, and the residue ignited. After dissolving in dilute acid, the quinalizarin test is applied.

In the determination of the total boron of plants, the plant tissue is ignited to a gray ash which is taken up with dilute acid. The quinalizarin test is then applied to some of the clarified extract.

A considerable number of soils, some of which had been fertilized with borax, and plants variously fertilized with boron were analyzed. The results obtained were fairly consistent with the treatments given. The test for available boron of soils appears to be well adapted for determining the boron status of a soil.



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Volume-Shape Factor of Particulate Matter

Probable Errors in the Computation

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THE volume of an aggregate of irregularly shaped particles can be determined from their average diameter by the simple relation

$$V = \delta ND^3$$

(1)

where  $\delta$  is the volume-shape factor (for spheres =  $\pi/6$ ),  $N$  the number of particles, and  $D$  the average diameter. The value of  $\delta$  is always less than  $\pi/6 = 0.5236$ , and depends upon characteristics of the material, its mode of cleavage during crushing, and perhaps to some extent the particle size. The shape factor of small particles should approximate that for a sphere as their particle size decreases, particularly since the methods used for the measurement of their diameters frequently does not distinguish any dominant irregularities. However this may be, there are data to warrant the assumption that a representative sample of an aggregate has a fairly constant shape factor (1, 3). This paper furnishes experimental evidence of the variation in shape factor for crushed quartz particles between the range of 10- and 40-mesh Bureau of Standards calibrated screens.

Two sieve sizes were used in the experiments described—namely, those particles passing a 10-mesh sieve and retained on a 20-mesh, and those passing this and retained on a 40-

mesh. The sizes of sieve openings were: 10-mesh, 0.2 cm.; 20-mesh, 0.084 cm.; and 40-mesh, 0.042. The sample was taken from the sieve and stored in a glass container. When aliquots were to be counted and weighed in accordance with the procedure discussed below, the total sample was placed upon a sheet of glazed paper and quartered.

The particles were carefully sieved and average diameters of upwards to 1000 particles in each sample determined by the technique developed by Hatch and Choate (3). The diameters of particles having an average volume were 0.214 and 0.089 cm., indicating rather significant differences from the sieve sizes given above. (Logarithmic mean sizes of the corresponding samples are  $0.19 \pm 0.05$  and  $0.089 \pm 0.05$  cm.) These differences have been discussed at length by Hatch in a paper on the determination of average size from sieve analysis (2). No significant variations were found in the particle sizes for each of the two samples for aliquots less than 1000 but more than 100 particles. Thus, the average diameters may be assumed as representative of the aggregates in question.

To determine the variation in shape factor, portions of each sample were weighed and counted and the average weight of each particle was calculated. This procedure

TABLE I. AVERAGE WEIGHT OF QUARTZ PARTICLES PASSING 10-MESH AND RETAINED ON 20-MESH

Weight of Particles	Number of Particles	Average Weight per Particle	Deviation	Deviation <sup>2</sup>
Grams		10 <sup>-5</sup> gram	10 <sup>-5</sup>	10 <sup>-10</sup>
0.5572	128	435	- 2	4
0.9811	187	525	+88	7744
2.0674	443	467	+30	900
2.0979	495	424	-13	169
2.4995	472	530	+93	8649
4.0260	947	425	-12	144
4.1882	930	450	+13	169
4.2124	1028	409	-28	784
4.2855	1090	393	-44	1936
4.8081	1284	374	-63	3969
5.5026	1111	495	+58	3364
6.0034	1521	395	-42	1764
9.1695	2084	440	+ 3	9
17.6686	4170	424	-13	169
17.6951	4139	428	- 9	81
17.8439	4455	401	-36	1296
17.8482	4396	406	-31	961

Average weight per particle =  $\frac{7421}{17} \times 10^{-5} = 437 \times 10^{-5}$  gram.

Standard deviation =  $\pm \sqrt{\frac{31,112}{17}} \times 10^{-5} = \pm 428 \times 10^{-6}$  gram.

Probable error of any determination =  $428 \times 10^{-6} \times 0.6745 = 301 \times 10^{-6} = 6.9\%$ .

TABLE II. AVERAGE WEIGHT OF QUARTZ PARTICLES PASSING 20-MESH AND RETAINED ON 40-MESH

Weight of Sample	Number of Particles	Average Weight per Particle	Deviation	Deviation <sup>2</sup>
Grams		10 <sup>-6</sup> gram	10 <sup>-6</sup>	10 <sup>-12</sup>
0.8805	3500	252	-18	324
0.8844	3500	253	-17	289
0.9366	3600	260	-10	100
0.9889	3700	267	- 3	9
0.9962	3600	276	+ 6	36
1.0014	4150	241	-29	841
1.0037	3700	271	+ 1	1
1.0069	3800	265	- 5	25
1.0310	3600	287	+17	289
1.0324	4230	245	-25	625
1.0413	3800	274	+ 4	16
1.0504	3679	285	+15	225
1.0920	4228	258	-12	144
1.1125	3529	300	+30	900
1.1171	3800	294	+24	576
2.0010	6817	293	+23	529
2.1484	8030	268	- 2	4
3.0039	11328	265	- 5	25
4.0189	14779	272	+ 2	4
5.0043	18129	276	+ 6	36

Average weight per particle =  $\frac{5402}{20} \times 10^{-6} = 270 \times 10^{-6}$  gram.

Standard deviation =  $\pm \sqrt{\frac{4998}{20}} \times 10^{-6} = \pm 50 \times 10^{-6}$ .

Probable error =  $50 \times 10^{-6} \times 0.6745 = 33.7 \times 10^{-6} = 12.5\%$ .



is in itself a measure of the shape factor, since the weight of the particles is obtained from Equation 1 by multiplying by the density

$$W = \delta \rho ND^3 \quad (2)$$

Since  $D$  and  $\rho$  are known and may be considered constant,

$$\delta = K \frac{W}{N} \quad (3)$$

Hence, the shape factor is as accurate as the average weight of the particles constituting the sample. Average particle weights were obtained by counting all particles from several portions of each sample, and reweighing. The results of this procedure are given in Tables I and II.

The tables show that the average particle weights as determined above are not constant. Nor does there appear to be any trend toward constancy, even when large numbers of particles are counted. The probable errors of individual samples are 6.9 and 12.5 per cent, which may be considered as being rather large.

The shape factors calculated from Equation 1 for the samples in question are 0.17 and 0.15, respectively (taking  $\rho = 2.65$ ). These values correspond with the shape factors determined by Hatch and Choate for very small particles (3). These investigators obtained volume-shape factors as low as 0.14 for particles of the order of 10 microns (0.001 cm.). Actual particle counts, however, were not made, but obtained by an indirect procedure.

Without question, the size distribution of the aggregate is most important. A small number of large particles can alter the ratio of  $W/N$  although no significant change in the size distribution, and hence the average diameter, is apparent. The volume of a particle is as the cube of the diameter. Hence, a single particle of an aggregate with a diameter 10 times that of the smallest has a volume (and mass) equivalent to 1000 particles of the latter. This fact undoubtedly accounts for the differences in average particle weights. (As a matter of experiment, the extremes of size-frequency plots vary from sample to sample without materially affecting the average or the median sizes.) It is questionable whether a size-weight distribution for calculating average diameters would yield better results since, as Hatch has pointed out, summation curves by weight and count will plot as parallel lines on logarithmic probability paper (2). It may be concluded, therefore, that the best value of the volume-shape factor is that determined from the average particle weights of several aliquots of the aggregate, each including a large number of particles.

### Acknowledgment

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# Judging Adhesiveness of Bitumen to Silica Sand

## A Comparison of Mixing Method and Wash Test

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THE fact that a certain parallelism exists between wetting and adhesiveness phenomena has tempted a number of investigators to apply the principles and methods of flotation to the problem of testing and improving the adhesiveness of bitumen to mineral aggregate. The inherent theoretical and practical limitations of such an undertaking have been outlined previously (4). Here it need only be mentioned that while wetting phenomena are usually instantaneous, the development of maximum adhesion between a mineral surface and bituminous material is a function of time. A recent contribution applying flotation principles to the problem of bitumen adhesion is the work of McLeod (2), who while using activators and wetting agents assumes that the ease of covering wet Ottawa sand with asphaltic bitumen is a measure of adhesiveness. Since the ease and speed with which the mixing test by McLeod can be performed would represent an advantage over the more lengthy procedure of the commonly used wash test (1, 3, 5), it appeared desirable to compare results of these two tests on the same set of samples.

### Experimental Procedure

The testing procedures used were the mixing method as reported by McLeod and the wash test with a machine previously described by the authors (5). For the experiments on mixing, Ottawa sand was thoroughly washed with distilled water and dried, and the fraction passing No. 8 and retained on a No. 40 sieve was employed. Two asphaltic materials having the properties given in Table I, and 0.05  $N$  solutions of sodium oleate and activator salts, respectively, were used for the tests. A

preliminary experiment showed that various MC and SC oils had different mixing efficiencies with the sand in the presence of water. However, the addition of from 0.2 to 0.5 cc. of 0.05  $N$  sodium oleate solution to any of the asphalt-sand-water mixtures resulted in a complete stripping of the coated sand and the balling up of the asphalt into numerous particles. The addition, thereafter, of the activator solutions had different effects, varying with the concentration and type of compound. The mixtures for testing adhesion were made in the following manner:

Thirty grams of sand and 1 gram of asphaltic material were thoroughly mixed in the presence of water, enough water being added to cover the sand and the excess drained off.

TABLE I. PROPERTIES OF ASPHALTS

	Slow-Curing Road Oil	
	No. 1	No. 2
Saybolt-Furol viscosity at 122° F., sec.	171	327
Specific gravity, 60° F./60° F.	1.0402	0.9766
Flash point, ° F.	240	260
Oliensis	Positive	Negative
Residue, %	71.8	73.2
Penetration of residue at 77° F., 100 grams, 5 sec.	86	85
Ductility of residue at 77° F., cm.	101	150+
Loss on heating 50 grams 5 hours at 325° F., %	9.92	8.36

Varying degrees of coverage were obtained.

One-half cubic centimeter of 0.05  $N$  sodium oleate was added and the mixture stirred; complete stripping occurred.

The activator solution was added in 0.1-cc. increments with thorough mixing after each addition until the sand was uniformly coated or until it was seen that no coating would be accomplished.



The adhesion data and mixing observations are given in Table II. The adhesiveness tests were made after the samples had cured in air 3 days and then stood in water one day.

Results

Asphalt 1, when mixed with the sand in the absence of water, wetting, and activating agents gave a very good coating, and after the same curing period as described above gave the best possible adhesion. Mixed in the presence of water, the mixing was still very good, whereas after the same curing period as above the asphalt stripped at 60° C., being not affected at 30° and 45° C., which can be called fair adhesion.

Asphalt 2, when mixed with the sand in the absence of water, wetting, and activating agents, gave a poor mix and poor adhesion. Mixing and adhesion were also very poor when this asphalt and sand were mixed in the presence of water.

These two asphalts provide the two extremes for observation—e. g., very good and very poor adhesion. The data in Table II indicate a similarity in the results of mixing observations and adhesion tests if both activator and wetting agent are used. There is, however, no exact correlation, because several mixes which were very good on the basis of efficient mixing gave poor adhesion. These cases are magnesium chloride and silver nitrate with asphalt 2. These two salts also lowered the adhesion of asphalt 1.

Since the wetting agent (sodium oleate) in the absence of an activator caused the complete stripping of the asphalts from the sand, the effect of omitting the wetting agent and adding only the so-called activator solution was investigated. Results of these experiments are given in Table III. In this case, the amount of water present is more important than where the activator and wetting agent are used.

These tests indicate that the salt solutions which are bad with soap are also bad when soap is not used. However, some of the salt solutions which have a good effect in connection with soap do not give good results when soap is not used. Lead nitrate appeared to be the best reagent in regard to both mixing and adhesion results, although potassium aluminum sulfate was almost as good. Calcium chloride, magnesium chloride, and silver nitrate were generally not good with regard to adhesion, although magnesium chloride and silver nitrate tended in proper amounts to give good mixing (with soap). Ferric chloride used without soap gave

TABLE III. RESULTS USING ACTIVATOR AND OMITTING WETTING AGENT

Reagent	0.05 N Cc.	H <sub>2</sub> O Cc.	Mix	30°	45°	60°	70°
Asphalt 1							
Co(NO <sub>3</sub> ) <sub>2</sub>	1	7	Medium	1	1	1	1
	5	3	Medium	1	1	1	1
MgCl <sub>2</sub>	1	7	Poor	1	1	1	1
	5	3	Poor	1	1	1	1
CaCl <sub>2</sub>	1	7	Poor	1	1	1	1
	5	3	Poor	1	1	1	3
BaCl <sub>2</sub>	1	7	Medium	1	1	1	3
	5	3	Medium	1	1	1	1
Pb(NO <sub>3</sub> ) <sub>2</sub>	1	7	Very good	1	1	1	1
	5	3	Very good	1	1	1	1
KAl(SO <sub>4</sub> ) <sub>2</sub>	1	7	Very good	1	1	1	1
	5	3	Very good	1	1	1	1
CuSO <sub>4</sub>	1	7	Very good	1	1	1	1
	5	3	Very good	1	1	1	3
FeCl <sub>3</sub>	1	7	Good	1	1	1	1
	5	3	Poor	1	1	1	1
AgNO <sub>3</sub>	1	7	Good	1	1	2	3
	5	3	Good	1	1	1	1
ZnSO <sub>4</sub>	1	7	Very good	1	1	3	..
	5	3	Very good	1	1	3	..
None	..	None	Very good	1	1	1	1
	..	8	Very good	1	1	3	..
Asphalt 2							
CaCl <sub>2</sub>	1	7	Poor	3	..	..	..
	5	3	Poor	3	..	..	..
KAl(SO <sub>4</sub> ) <sub>2</sub>	1	7	Poor	1	3	..	..
	5	3	Poor	1	1	1	1
Pb(NO <sub>3</sub> ) <sub>2</sub>	1	7	Poor	1	1	1	3
	5	3	Poor	1	1	1	1
BaCl <sub>2</sub>	1	7	Poor	1	1	1	1
	5	3	Poor	1	1	1	1
AgNO <sub>3</sub>	1	7	Poor	3	..	..	..
	5	3	Poor	1	3	..	..
FeCl <sub>3</sub>	1	7	Poor	1	1	1	1
	5	3	Poor	1	1	1	1
CuSO <sub>4</sub>	1	7	Poor	3	..	..	..
	5	3	Good	1	3	..	..
MgCl <sub>2</sub>	1	7	Poor	3	..	..	..
	5	3	Poor	3	..	..	..
Co(NO <sub>3</sub> ) <sub>2</sub>	1	7	Poor	3	..	..	..
	5	3	Poor	3	..	..	..
None	..	8	Poor	3	..	..	..
	..	None	Poor	3	..	..	..

good mixing when added in very small quantities, but as the quantity was increased the mixing efficiency decreased. However, any particles which were coated in the presence of ferric chloride gave very good adhesion.

Conclusions

The ease of covering a sand with a bituminous material by means of simple mixing may be a general indication, but is not a dependable measure of the adhesion relationship between the bitumen and the sand.

The best agreement of the mixing test data with those from the wash test occurs where wetting agents are used in conjunction with aluminum, iron, and lead ions—i. e., with those ions which are generally recognized as favorably affecting adhesion of bitumen to aggregate. For such cases and where the aggregate has to be coated in the wet condition with the help of soap-type activators the McLeod test appears to have some merit.

The mixing test cannot be substituted for the wash test if definite information on the adhesion relationship between bitumen and aggregate is desired.

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TABLE II. MIXING AND ADHESION DATA

(0.5 cc. of sodium oleate used)

Soap	Salt	Salt Solution, Cc.	Mix	Adhesion Value <sup>a</sup>			
				30°	45°	60°	70°
Asphalt 1							
1	Co(NO <sub>3</sub> ) <sub>2</sub>	0.2	Uniform	1	1	1	1
2	KAl(SO <sub>4</sub> ) <sub>2</sub>	0.1	Uniform	1	1	1	1
3	FeCl <sub>3</sub>	0.1	Uniform	1	1	1	1
4	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.1	Uniform	1	1	1	1
5	ZnSO <sub>4</sub>	0.2	Uniform	1	1	1	1
6	AgNO <sub>3</sub>	0.9	Uniform	1	1	1	3
7	CaCl <sub>2</sub>	0.5	Uniform	1	1	3	3
8	BaCl <sub>2</sub>	0.2	Uniform	1	1	1	1
9	MgCl <sub>2</sub>	0.5	Uniform	1	1	1	3
10	CuSO <sub>4</sub>	0.2	Uniform	1	1	1	1
Asphalt 2							
Coating							
1	Co(NO <sub>3</sub> ) <sub>2</sub>	0.2	Uniform	1	1	1	1
2	KAl(SO <sub>4</sub> ) <sub>2</sub>	0.1	Uniform	1	1	1	1
3	FeCl <sub>3</sub>	0.3	Uniform	1	1	1	1
4	Pb(NO <sub>3</sub> ) <sub>2</sub>	0.1	Uniform	1	1	1	1
5	ZnSO <sub>4</sub>	0.2	Uniform	1	1	1	1
6	AgNO <sub>3</sub>	1.2	Poor until 1.2 cc. were added	3	..	..	..
7	CaCl <sub>2</sub>	2.1	Very poor	3	..	..	..
8	BaCl <sub>2</sub>	0.1	Good	1	1	1	1
9	MgCl <sub>2</sub>	0.5	Poor until 5 cc. were added	2	3	..	..
10	CuSO <sub>4</sub>	0.1	Uniform	1	1	1	1

<sup>a</sup> 1 = no stripping, 2 = 25% or less stripped, 3 = more than 25% stripped.



# A Table for Ebulliometers

## For Use with Alcoholic Liquids Containing Solid Matter

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THE ebulliometer is used in many industrial plants such as wineries, breweries, and distilleries for rapid determination of the alcohol content of wine, beer, mash, and distilled liquors. The tables or scales which accompany the ebulliometers are constructed for liquids containing either no solid matter or one rather definite quantity of solids such as would be found in beer or light wine.

Since the variety of alcoholic liquids which the ebulliometer may be called upon to analyze is rather large and may cover solid contents of considerable range, a table which takes into account such solid matter may be of value.

To obtain data with which to construct such a table, mixtures of 192-proof alcohol, sucrose, and distilled water were prepared containing approximately 1, 3, 5, 7, 9, and 11 per cent of alcohol by volume accurately determined by a pycnometer, and 0, 2, 4, 6, 8, and 10 grams of sucrose per 100 ml.—a total of 36 solutions. Dilutions were made with a buret and a volumetric flask which were checked against each other, and the liquids were measured at 20° C.

Each solution was tested, simultaneously, in a Juerst and a Salleron ebulliometer. The thermometer used with the Juerst was manufactured by the Taylor Instrument Company, was graduated the same as the Juerst thermometers, and was certified by the National Bureau of Standards. The thermometer used with the Salleron was the one furnished with the ebulliometer,

and although it had not been certified by the National Bureau of Standards, it agreed very closely with the Taylor instrument. In a third ebulliometer, water was kept boiling continuously to detect any change in boiling point during the periods of testing.

Before each series of tests, the ebulliometers were cleaned by boiling with a strong solution of alkali to remove the film of solid matter which collects inside the boiler after only a few tests are made and which causes bumping. Solutions containing more than 10 grams per 100 ml. of sucrose were not used because of the tendency of liquids of high-solid content to bump. Such liquids are best analyzed by diluting the samples. Even after thorough washing of the boiler, the first boiling point of water was usually different from the succeeding ones; therefore the boiling point of water was obtained by boiling successive portions of water until several duplicate results were obtained.

The boiler was then thoroughly rinsed with the alcoholic liquid to be tested, but in spite of that fact, the boiling point of the solution was affected by the previous presence of water and the first reading had to be discarded, as it was usually high, corresponding to a percentage of alcohol which was too low.

The boiling point of each solution was determined at least six times with each ebulliometer. The readings were made by observing the thermometers every 15 seconds from the time boiling started until the mercury remained constant during several observations. The point at which the mercury was

TABLE I. BOILING POINT DIFFERENCES, JUERST EBULLIOMETER

Alcohol %	Grams of Sucrose per 100 ML. of Solution					
	0	2	4	6	8	10
0.9585	0.95	0.92	0.89	0.86	0.83	0.82
2.8755	2.68	2.68	2.69	2.72	2.67	2.70
4.7925	4.20	4.23	4.22	4.25	4.27	4.30
6.7095	5.60	5.65	5.66	5.71	5.73	5.76
8.6265	6.83	6.91	6.92	7.02	7.07	7.12
10.5435	7.96	8.02	8.12	8.19	8.17	8.27

TABLE II. ADJUSTED RESULTS USED IN CONSTRUCTING A TABLE, JUERST EBULLIOMETER

Alcohol %	Grams of Sucrose per 100 ML. of Solution					
	0	2	4	6	8	10
0.9585	0.95	0.92	0.89	0.86	0.83	0.80
2.8755	2.68	2.68	2.68	2.68	2.68	2.68
4.7925	4.20	4.22	4.24	4.26	4.28	4.30
6.7095	5.60	5.63	5.66	5.69	5.72	5.75
8.6265	6.82	6.88	6.94	7.00	7.06	7.12
10.5435	7.96	8.02	8.08	8.14	8.20	8.26

TABLE III. BOILING POINT DIFFERENCES, SALLERON EBULLIOMETER

Alcohol %	Grams of Sucrose per 100 ML. of Solution					
	0	2	4	6	8	10
0.9585	0.94	0.92	0.89	0.88	0.85	0.84
2.8755	2.68	2.68	2.69	2.70	2.70	2.70
4.7925	4.20	4.23	4.26	4.29	4.31	4.35
6.7095	5.60	5.65	5.66	5.71	5.77	5.81
8.6255	6.84	6.90	6.92	6.96	7.06	7.10
10.5435	7.96	8.02	8.09	8.16	8.17	8.26

TABLE IV. ADJUSTED RESULTS, SALLERON EBULLIOMETER

Alcohol %	Grams of Sucrose per 100 ML. of Solution					
	0	2	4	6	8	10
0.9585	0.94	0.92	0.90	0.88	0.86	0.84
2.8755	2.69	2.69	2.69	2.69	2.69	2.69
4.7925	4.20	4.23	4.26	4.29	4.32	4.35
6.7095	5.60	5.64	5.68	5.72	5.76	5.80
8.6255	6.84	6.89	6.94	6.99	7.04	7.09
10.5435	7.95	8.01	8.07	8.13	8.19	8.25

TABLE V. READINGS WITH JUERST EBULLIOMETER

Sucrose Grams/100	Alcohol ml. % by volume	Boiling Point Difference Found	High	Low	Variation
0	0.9585	0.95	0.95	0.94	0.01
0	2.8755	2.68	2.69	2.67	0.02
0	4.7925	4.20	4.22	4.19	0.03
0	6.7095	5.61	5.63	5.59	0.04
0	8.6265	6.83	6.85	6.82	0.03
0	10.5435	7.98	7.99	7.97	0.02
2	0.9585	0.92	0.93	0.92	0.01
2	2.8755	2.68	2.69	2.67	0.02
2	4.7925	4.23	4.24	4.22	0.02
2	6.7095	5.65	5.68	5.62	0.06
2	8.6265	6.91	6.93	6.87	0.06
2	10.5435	8.04	8.05	8.03	0.02
4	0.9585	0.89	0.89	0.90	0.01
4	2.8755	2.69	2.70	2.67	0.03
4	4.7925	4.22	4.25	4.20	0.05
4	6.7095	5.66	5.70	5.63	0.07
4	8.6265	6.92	6.93	6.90	0.05
4	10.5435	8.12	8.14	8.10	0.04
6	0.9585	0.86	0.87	0.85	0.02
6	2.8755	2.72	2.73	2.70	0.03
6	4.7925	4.25	4.27	4.22	0.05
6	6.7095	5.71	5.74	5.68	0.06
6	8.6265	7.02	7.04	7.00	0.04
6	10.5435	8.19	8.21	8.18	0.03
8	0.9585	0.83	0.84	0.82	0.02
8	2.8755	2.67	2.70	2.63	0.07
8	4.7925	4.27	4.30	4.23	0.07
8	6.7095	5.73	5.76	5.71	0.05
8	8.6265	7.07	7.11	7.03	0.08
8	10.5435	8.17	8.18	8.13	0.05
10	0.9585	0.82	0.84	0.81	0.03
10	2.8755	2.70	2.71	2.68	0.03
10	4.7925	4.30	4.32	4.26	0.06
10	6.7095	5.76	5.78	5.73	0.05
10	8.6265	7.12	7.15	7.10	0.05
10	10.5435	8.27	8.29	8.24	0.05

TABLE VI. FORMULAS FOR CALCULATING EBULLIOMETER TABLE  
(Figures in first column represent grams of sucrose per 100 ml. of solution)

0	$y = 0.98469x + 0.03004x^2 + 0.00158x^3$
2	$y = 1.00618x + 0.02088x^2 + 0.00219x^3$
4	$y = 1.03436x + 0.00997x^2 + 0.00291x^3$
6	$y = 1.05861x + 0.00072x^2 + 0.00348x^3$
8	$y = 1.08209x - 0.00817x^2 + 0.00402x^3$
10	$y = 1.11577x - 0.02054x^2 + 0.00484x^3$



stationary for the longest period was recorded and the total of such readings averaged. Readings were estimated to hundredths of a degree on each thermometer. Results obtained, in boiling point differences, are shown in Table I for the Juerst and in Table III for the Salleron. Since these figures were slightly irregular, they were adjusted so that when plotted, smooth curves would be obtained. Table II shows the adjusted results used for constructing the table for

the Juerst ebulliometer. The adjusted results for the Salleron, shown in Table IV, were so nearly like the corresponding ones for the Juerst that one table was considered satisfactory for both ebulliometers. Table V shows the highest and lowest readings obtained for each solution and proves that consistent results can be obtained by using care in all of the manipulations. The variations in individual readings on the Salleron thermometer were larger than those on the Juerst because the

TABLE VII. TABLE TO ACCOMPANY EBULLIOMETER

(Per cent of alcohol by volume corresponding to differences in boiling points for quantities of sucrose between 0 and 10 grams per 100 ml.)													
Boiling Point Difference	Grams of Sucrose per 100 Ml. of Solution						Boiling Point Difference	Grams of Sucrose per 100 Ml. of Solution					
	0	2	4	6	8	10		0	2	4	6	8	10
Per cent by volume							Per cent by volume						
-0.15	..	..	..	..	..	0.0	3.95	4.45	4.43	4.42	4.41	4.40	4.39
-0.10	..	..	..	..	0.01	0.04	4.00	4.52	4.50	4.48	4.47	4.46	4.45
-0.05	..	..	..	0.03	0.06	0.09	4.05	4.59	4.57	4.55	4.53	4.52	4.51
0.0	0.0	0.02	0.05	0.08	0.11	0.14	4.10	4.65	4.63	4.61	4.59	4.58	4.57
0.05	0.05	0.07	0.10	0.13	0.16	0.19	4.15	4.72	4.70	4.68	4.66	4.64	4.63
0.10	0.10	0.12	0.15	0.18	0.21	0.24	4.20	4.78	4.76	4.74	4.72	4.70	4.68
0.15	0.15	0.17	0.19	0.22	0.25	0.28	4.25	4.85	4.83	4.81	4.78	4.76	4.74
0.20	0.20	0.22	0.24	0.27	0.30	0.33	4.30	4.91	4.89	4.87	4.84	4.82	4.80
0.25	0.25	0.27	0.29	0.32	0.35	0.38	4.35	4.98	4.96	4.93	4.90	4.88	4.86
0.30	0.30	0.32	0.34	0.37	0.40	0.43	4.40	5.04	5.02	4.99	4.96	4.94	4.92
0.35	0.35	0.37	0.39	0.41	0.44	0.47	4.45	5.11	5.08	5.05	5.02	5.00	4.98
0.40	0.40	0.42	0.44	0.46	0.49	0.52	4.50	5.18	5.15	5.12	5.09	5.06	5.04
0.45	0.45	0.47	0.49	0.51	0.54	0.57	4.55	5.25	5.22	5.19	5.16	5.13	5.10
0.50	0.50	0.52	0.54	0.56	0.59	0.62	4.60	5.32	5.28	5.25	5.22	5.19	5.16
0.55	0.55	0.57	0.59	0.61	0.64	0.67	4.65	5.38	5.34	5.31	5.28	5.25	5.22
0.60	0.60	0.62	0.64	0.66	0.69	0.72	4.70	5.45	5.41	5.38	5.35	5.32	5.29
0.65	0.65	0.67	0.69	0.71	0.73	0.76	4.75	5.52	5.48	5.45	5.41	5.38	5.35
0.70	0.70	0.72	0.74	0.76	0.78	0.81	4.80	5.59	5.55	5.52	5.48	5.45	5.42
0.75	0.76	0.78	0.80	0.82	0.84	0.86	4.85	5.66	5.62	5.59	5.55	5.52	5.48
0.80	0.81	0.83	0.85	0.87	0.89	0.91	4.90	5.73	5.69	5.66	5.62	5.58	5.54
0.85	0.86	0.88	0.90	0.92	0.94	0.96	4.95	5.80	5.76	5.73	5.69	5.65	5.61
0.90	0.91	0.92	0.94	0.96	0.98	1.00	5.00	5.87	5.83	5.79	5.75	5.71	5.67
0.95	0.96	0.97	0.99	1.01	1.03	1.05	5.05	5.94	5.90	5.86	5.82	5.78	5.74
1.00	1.02	1.03	1.04	1.06	1.08	1.10	5.10	6.01	5.96	5.92	5.88	5.84	5.80
1.05	1.07	1.08	1.09	1.11	1.13	1.15	5.15	6.08	6.03	5.99	5.95	5.91	5.87
1.10	1.12	1.13	1.14	1.16	1.18	1.20	5.20	6.15	6.10	6.06	6.01	5.97	5.93
1.15	1.17	1.18	1.19	1.21	1.23	1.25	5.25	6.22	6.17	6.13	6.08	6.04	6.00
1.20	1.22	1.23	1.24	1.26	1.28	1.30	5.30	6.30	6.25	6.20	6.15	6.11	6.06
1.25	1.28	1.29	1.30	1.32	1.34	1.36	5.35	6.37	6.32	6.27	6.22	6.17	6.12
1.30	1.33	1.34	1.35	1.37	1.39	1.41	5.40	6.44	6.39	6.34	6.29	6.24	6.19
1.35	1.39	1.40	1.41	1.43	1.45	1.47	5.45	6.52	6.46	6.41	6.36	6.31	6.26
1.40	1.44	1.45	1.46	1.48	1.50	1.52	5.50	6.59	6.53	6.48	6.43	6.38	6.33
1.45	1.50	1.51	1.52	1.54	1.56	1.58	5.55	6.66	6.60	6.55	6.49	6.44	6.39
1.50	1.55	1.56	1.57	1.59	1.61	1.63	5.60	6.73	6.67	6.62	6.56	6.51	6.45
1.55	1.61	1.62	1.63	1.65	1.67	1.69	5.65	6.81	6.74	6.69	6.63	6.57	6.51
1.60	1.66	1.67	1.68	1.70	1.72	1.74	5.70	6.88	6.81	6.76	6.70	6.64	6.58
1.65	1.72	1.73	1.74	1.76	1.78	1.80	5.75	6.95	6.88	6.83	6.77	6.71	6.65
1.70	1.77	1.78	1.80	1.82	1.84	1.86	5.80	7.03	6.96	6.90	6.84	6.78	6.72
1.75	1.83	1.84	1.86	1.88	1.90	1.92	5.85	7.11	7.04	6.98	6.92	6.86	6.80
1.80	1.88	1.89	1.91	1.93	1.95	1.97	5.90	7.18	7.11	7.05	6.99	6.93	6.87
1.85	1.94	1.95	1.97	1.99	2.01	2.03	5.95	7.25	7.18	7.12	7.06	7.00	6.93
1.90	1.99	2.00	2.02	2.04	2.06	2.08	6.00	7.33	7.26	7.19	7.13	7.07	7.00
1.95	2.05	2.06	2.08	2.10	2.12	2.14	6.05	7.40	7.33	7.26	7.20	7.13	7.06
2.00	2.10	2.11	2.13	2.15	2.17	2.19	6.10	7.48	7.41	7.34	7.27	7.20	7.13
2.05	2.16	2.17	2.19	2.21	2.23	2.25	6.15	7.55	7.48	7.41	7.34	7.27	7.20
2.10	2.21	2.22	2.24	2.26	2.28	2.30	6.20	7.63	7.56	7.49	7.42	7.35	7.28
2.15	2.27	2.28	2.30	2.32	2.34	2.36	6.25	7.71	7.64	7.56	7.49	7.42	7.35
2.20	2.33	2.34	2.36	2.38	2.39	2.41	6.30	7.79	7.72	7.64	7.57	7.50	7.43
2.25	2.39	2.40	2.42	2.44	2.45	2.47	6.35	7.87	7.80	7.72	7.65	7.57	7.50
2.30	2.44	2.45	2.47	2.49	2.50	2.52	6.40	7.94	7.87	7.79	7.72	7.64	7.57
2.35	2.50	2.50	2.52	2.54	2.55	2.57	6.45	8.02	7.95	7.87	7.80	7.72	7.65
2.40	2.56	2.56	2.58	2.59	2.60	2.62	6.50	8.10	8.03	7.95	7.87	7.79	7.72
2.45	2.62	2.62	2.64	2.65	2.66	2.68	6.55	8.18	8.10	8.02	7.94	7.86	7.79
2.50	2.67	2.67	2.69	2.70	2.71	2.73	6.60	8.26	8.18	8.10	8.02	7.94	7.86
2.55	2.73	2.73	2.75	2.76	2.77	2.79	6.65	8.34	8.26	8.18	8.10	8.02	7.94
2.60	2.79	2.79	2.81	2.82	2.83	2.85	6.70	8.42	8.34	8.26	8.18	8.10	8.02
2.65	2.85	2.85	2.87	2.88	2.89	2.91	6.75	8.50	8.42	8.34	8.26	8.17	8.09
2.70	2.91	2.91	2.93	2.94	2.95	2.97	6.80	8.58	8.49	8.41	8.33	8.24	8.16
2.75	2.97	2.97	2.98	2.99	3.01	3.03	6.85	8.66	8.57	8.49	8.40	8.31	8.13
2.80	3.03	3.03	3.04	3.05	3.07	3.08	6.90	8.74	8.65	8.57	8.48	8.39	8.31
2.85	3.09	3.09	3.10	3.11	3.12	3.13	6.95	8.82	8.73	8.65	8.56	8.47	8.38
2.90	3.15	3.15	3.15	3.16	3.17	3.18	7.00	8.91	8.82	8.73	8.64	8.55	8.46
2.95	3.21	3.21	3.21	3.21	3.22	3.23	7.05	8.99	8.90	8.81	8.72	8.63	8.54
3.00	3.27	3.27	3.27	3.27	3.28	3.29	7.10	9.07	8.98	8.89	8.80	8.71	8.62
3.05	3.33	3.33	3.33	3.33	3.34	3.35	7.15	9.15	9.06	8.97	8.88	8.79	8.70
3.10	3.39	3.39	3.39	3.39	3.40	3.41	7.20	9.23	9.14	9.05	8.96	8.87	8.78
3.15	3.45	3.45	3.45	3.45	3.46	3.47	7.25	9.31	9.22	9.13	9.04	8.95	8.86
3.20	3.51	3.50	3.50	3.50	3.51	3.52	7.30	9.40	9.31	9.22	9.12	9.03	8.94
3.25	3.57	3.56	3.56	3.56	3.57	3.58	7.35	9.48	9.39	9.30	9.20	9.11	9.01
3.30	3.63	3.62	3.62	3.62	3.63	3.64	7.40	9.57	9.48	9.38	9.28	9.19	9.09
3.35	3.69	3.68	3.68	3.68	3.69	3.69	7.45	9.65	9.56	9.46	9.36	9.27	9.17
3.40	3.75	3.74	3.74	3.74	3.74	3.74	7.50	9.74	9.65	9.55	9.45	9.36	9.26
3.45	3.81	3.80	3.80	3.80	3.80	3.80	7.55	9.82	9.73	9.63	9.53	9.44	9.34
3.50	3.87	3.86	3.86	3.86	3.86	3.86	7.60	9.91	9.81	9.71	9.61	9.52	9.42
3.55	3.94	3.93	3.93	3.92	3.92	3.92	7.65	10.00	9.90	9.80	9.70	9.61	9.51
3.60	4.00	3.99	3.99	3.98	3.98	3.98	7.70	10.09	9.99	9.89	9.79	9.70	9.60
3.65	4.06	4.05	4.05	4.04	4.04	4.04	7.75	10.18	10.08	9.98	9.88	9.78	9.68
3.70	4.13	4.12	4.12	4.11	4.10	4.10	7.80	10.26	10.16	10.06	9.96	9.86	9.76
3.75	4.20	4.19	4.18	4.17	4.16	4.16	7.85	10.35	10.25	10.15	10.05	9.95	9.84
3.80	4.26	4.25	4.24	4.23	4.22	4.22	7.90	10.44	10.34	10.24	10.14	10.03	9.92
3.85	4.32	4.31	4.30	4.29	4.28	4.27	7.95	10.52	10.42	10.32	10.22	10.11	10.00
3.90	4.39	4.37	4.36	4.35	4.34	4.33	8.00	10.61	10.51	10.40	10.30	10.19	10.09



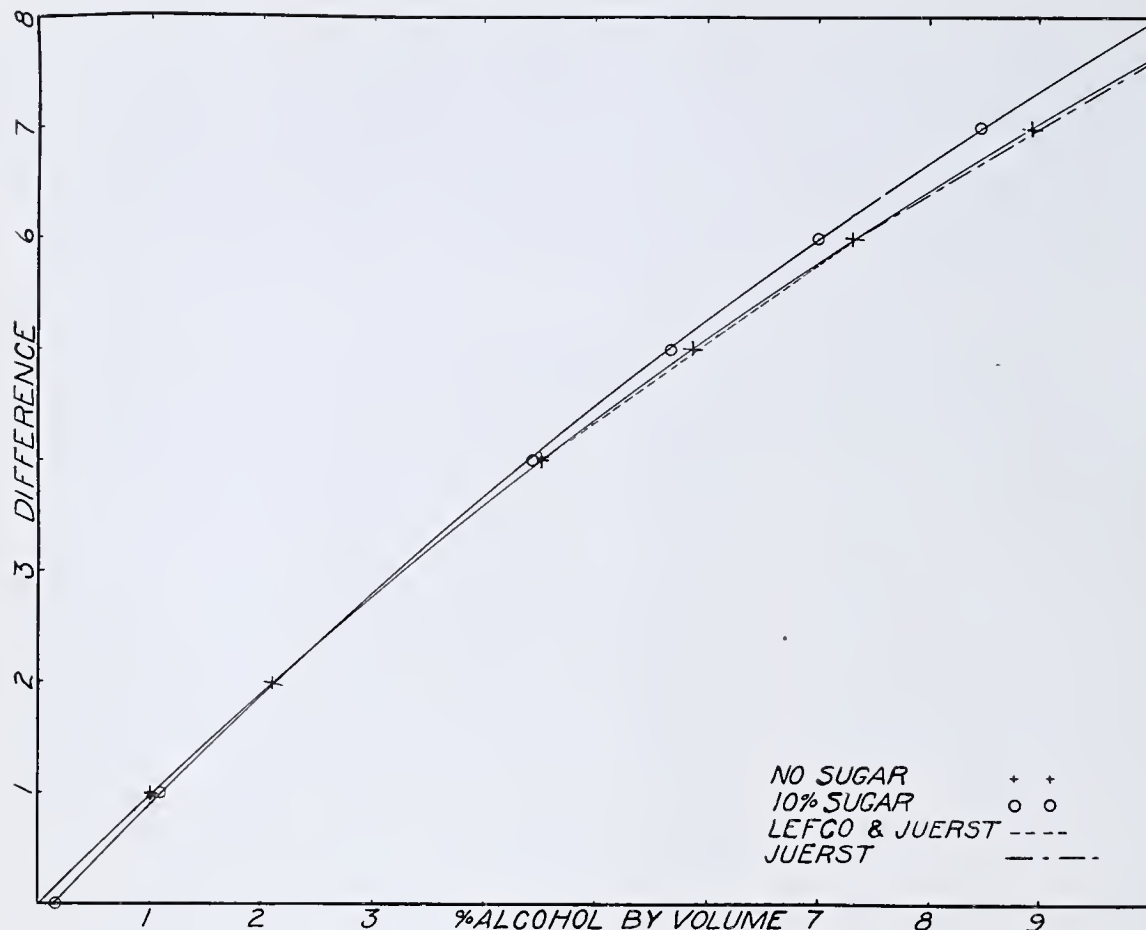


FIGURE 1

scale divisions of the Salleron are smaller and consequently more difficult to read.

A formula was obtained for each series of solutions containing the same quantity of sucrose, by use of the equation  $y = ax + bx^2 + cx^3$ , in which  $y$  is the difference between boiling points,  $x$  is the per cent of alcohol by volume, and  $a$ ,  $b$ , and  $c$  are constants whose values were calculated from the experimental data, by the method of least squares. These formulas are shown in Table VI. By their use Table VII was constructed, showing per cent of alcohol by volume, for each 0.05 degree difference between boiling points, from 0 to 8, for solutions containing 0, 2, 4, 6, 8, and 10 grams of sucrose per 100 ml. This table may be used with any ebulliometer whose thermometer is based on the Centigrade scale. Using boiling point differences as ordinates and percentage of alcohol as abscissas, the author plotted a curve for each quantity of sucrose used. These curves are shown in Figure 1.

The column of Table VII for solutions containing no sucrose agrees very well with the table which accompanies the Lefco ebulliometer (3) except at one point. When the boiling point differences in the Lefco table are plotted against percentages of alcohol, they form a smooth curve, except for the boiling point differences 4.00 to 6.00, where they form a straight line. Evidently the interpolations at that part of the table were made by proportion rather than by use of a formula. Almost exactly the same discrepancy is noticed at the corresponding part of the Juerst table (2).

At boiling point difference 6.20, Table VII and the Juerst table again begin to separate and at 7.75, the highest point on the Juerst scale, the discrepancy is 0.07 per cent alcohol. Repeated attempts to check the Juerst table at its upper limit were unsuccessful. Table VII agrees very well with the Lefco table at its upper limit. It is concluded that there is a small error in the Lefco table at boiling point difference 5.00 and in

the Juerst table at boiling point difference 5.00 and from 6.20 to 7.75.

A correction table (1) to be used for beer and beverages having a real extract (solids) of from 3 to 12 per cent gives a factor to be added to the alcohol found, according to the amount of solids present. It agrees exactly with Table VII at 5.66 per cent alcohol, for the various percentages of sucrose, but it cannot be used for liquids containing other percentages of alcohol.

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- (2) U. S. Internal Revenue Regulations, 7, Table VII.
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## A Modified Jones Reductor

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THE Jones reductor is a convenient apparatus for effecting the reduction of certain compounds. Its efficiency in certain cases, however, is governed by the rate at which the solution containing the substance to be reduced flows through the reductor. A definite rate of flow through a Jones reductor equipped with an ordinary stopcock can be obtained only by trial and error; furthermore, duplicate rates are practically impossible.

The modified Jones reductor herein described enables one to obtain a definite and constant rate of flow. This may be accomplished by fitting the delivery tube of the reductor with replaceable ground-glass capillary tubes of various-sized orifices.

The tip of the delivery tube is first expanded to form the female joint. A 15-cm. (6-inch) length of capillary tubing, possessing an inside diameter of 1.5 mm. and an outside diameter approximately equal to that of the delivery tube of the reductor, is heated at one end until the orifice is barely closed. The capillary tube is then heated at a point 5 cm. (2 inches) from the closed end and drawn out until it possesses a taper simulating that of the female cone. The male cone is obtained by cutting the tubing at the constriction. Three or four male cones should be made and ground into the delivery tube of the reductor, care being taken not to grind too long on any one cone before grinding in the next. In this way all the cones are gradually ground to the same size and may be used interchangeably in the reductor. The closed tips of the cones are then ground down on a piece of plate glass until each cone possesses the desired orifice size. In this way cones delivering approximately 20, 50, 100, or any desired number of milliliters per minute may be obtained. The volume delivered must be determined by trial. If too large a volume is delivered, the orifice may be closed slightly by reheating the tip.



# Device for Subliming Iodine

JACOB CORNOG AND LEONARD OLSON

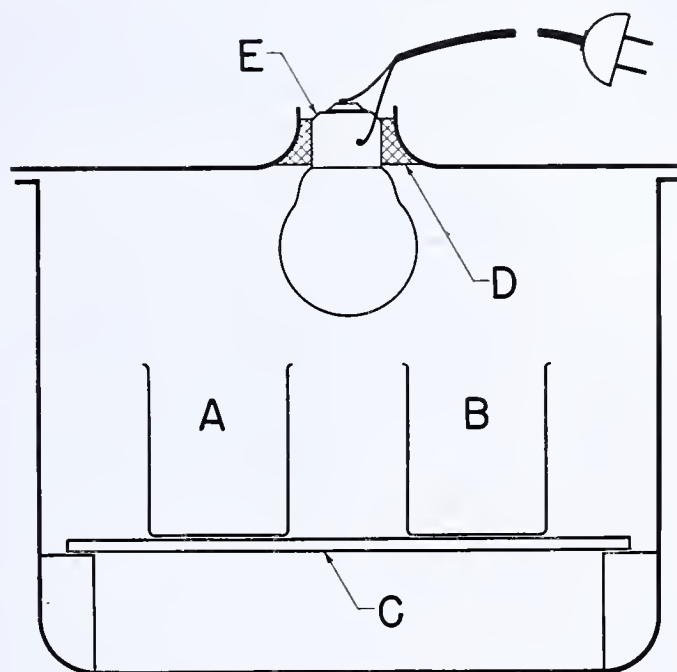
University of Iowa, Iowa City, Iowa

MANY books on analytical chemistry give directions for subliming iodine in quantities of a few grams, but the authors have not found in the literature a description of a device that may be assembled from materials found in most laboratories and used for subliming iodine in lots ranging up to 500 grams (1 pound) in weight. Such a device is described in this article.

As indicated in the figure, the device consists of a desiccator of Pyrex glass, having a diameter of approximately 250 mm., and bearing a 40- to 60-watt light bulb in the lid. Lead wires from an ordinary municipal lighting circuit are soldered to the metallic base, *E*, of the bulb, which is sealed in the hole in the desiccator lid with plaster of Paris, *D*, in such a way that no metallic surface is exposed to the interior of the desiccator and also so that the plaster does not touch the wire soldered to the central terminal of the bulb, which is covered with de Khotinskiv or a similar cement. The tile, *C*, supports the beaker or evaporating dish, *A*, containing the iodine to be sublimed and the beaker, *B*, containing a drying agent such as phosphorus pentoxide. If a resistance is placed in series in the external circuit, closer regulation of heating temperatures is assured.

When a current is passed through the bulb, the top of the desiccator becomes warmer than the bottom and iodine vaporizes and condenses on the lower sides and the bottom. The rate of sublimation may be increased by using devices which increase the difference in temperature existing between the upper and lower parts of the desiccator, such as insulating the top or cooling the bottom of the desiccator.

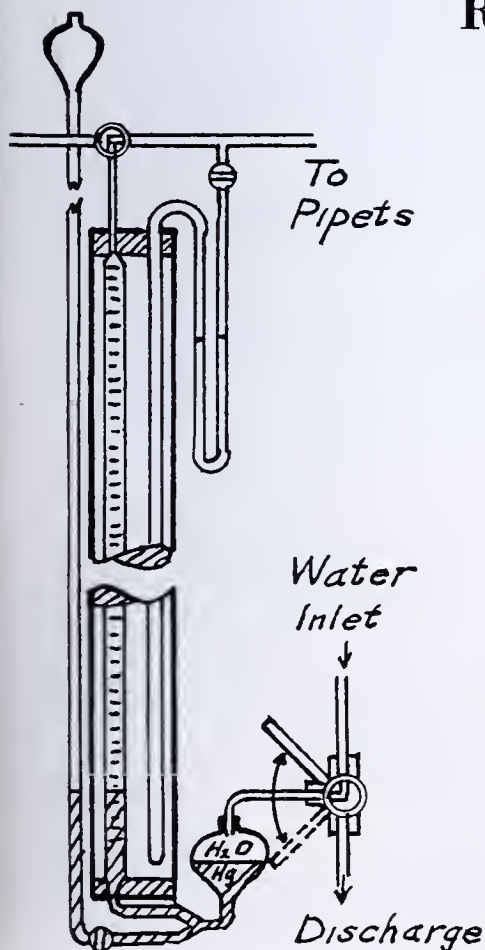
This apparatus has found a variety of uses in this laboratory, such as drying and subliming iodine recovered from accumulated iodine "residues" by wet methods, recovering



iodine mixed with broken glass and dirt resulting from the breaking of bottles in transit or by dropping them on the floor, and in the drying and purification of substances, such as iodine monochloride, that are volatile, corrosive, and easily decomposed at relatively low temperatures.

## Rapid Operating Device for Orsat Apparatus

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THE operation of ordinary gas analysis equipment is somewhat tedious and requires the constant attention of the analyst. Automatic absorption pipets (1, 2, 3) and a hydraulically operated device for transporting the mercury bulb (4) have been suggested to decrease the time consumed and to relieve the operator during a portion of the analysis. Each has a advantageous application.

A study of the operation of a standard analysis procedure will indicate that a large portion of the total time is used in returning pipet solutions to their original marks, balancing the pressure, and reading the buret. These operations are complicated by the fact that the confining liquid in the buret is not perfectly controlled, but is free to surge between the buret and the leveling bulb, and cannot be brought to rest quickly.

The device described below permits a positive control on the confining liquid (mercury must be used) by the presence of an incompressible fluid (water) over the mercury in the leveling bulb. This means of control so facilitates the operation of any type of gas analysis equipment that considerable saving of time should result. In the analysis of coal-mine air (carbon dioxide, oxygen, carbon monoxide, methane) with a standard laboratory-type apparatus, using contact and slow-combustion pipets, the total time of analysis may be cut in half with this device.

### Description

The essential difference between this device and the conventional Orsat apparatus is that the motivating force here is water pressure which is applied over the mercury in the leveling bulb. This change necessitates the use of a leveling tube (a tube parallel to the buret, open at the top and connected at the bottom to the buret and to the leveling bulb) so that an estimate of the pressure in the buret may be obtained if desired. The usual long rubber



tube connecting the leveling bulb to the buret is replaced by short lengths of glass tubing connecting the leveling bulb to the buret and to the leveling tube. A stopcock is inserted between the leveling bulb and the leveling tube.

Water at a pressure slightly in excess of that required to raise the mercury to the top of the buret may be conveniently supplied through a reducing valve from the laboratory tap. Higher pressures than needed might prove dangerous and would make manipulation difficult. The water is led into the top of the leveling bulb through a three-way plug valve, the third side of which is connected to the drain. By rotating this valve through a 90-degree arc the direction of flow of mercury in the buret is reversed. At the center of the arc the mercury is held stationary.

The ease and speed of manipulation depend to a large extent on the functioning of this valve. As a suitable valve was not available at any of the equipment houses in the neighborhood of the author's laboratory, a standard three-way 0.25-inch brass plug valve was remodeled. The plug was filled with solder and drilled to form an L-shaped port only 0.09 inch in diameter. A slight groove in the surface was tapered into each end of the drill hole, as is sometimes done with glass stopcocks, to provide for a more readily adjustable flow. Grooves were then machined about the circumference of the top and bottom of the plug to provide for lubrication. As a lubricant, automobile water-pump grease was found superior to any of the common laboratory greases. All water connections were made with copper tubing 0.25 inch in outside diameter.

Because of the more accurate control that may be maintained on the mercury level in the buret, it is possible to replace the conventional mercury manometer with one of water. This makes leveling off somewhat easier and increases the accuracy of the apparatus. The flow of water over the mercury in the leveling bulb serves to keep the mercury clean, and it has not

been necessary throughout the analysis of over a thousand samples of mine air to provide any additional cleaning.

### Operation

Operation is similar to the conventional procedure except that the mercury is raised in the buret by passing water into the top of the leveling bulb instead of raising the leveling bulb. In leveling off, the mercury level in the leveling tube is adjusted to approximately that in the buret. Then the stopcock is closed to the leveling tube, the stopcock to the water manometer opened, and the pressure balanced with that in a conventional compensating tube.

After the operator is familiar with the apparatus, an estimate of pressure may be obtained from returning the solutions in the absorption pipets to their original marks and the use of the leveling tube may be largely eliminated, affording an additional saving of time.

This equipment, in addition to saving time, takes much of the drudgery out of routine analysis by eliminating the continual raising and lowering of the mercury-filled leveling bulb. It is particularly well suited to procedures that require a slow or even flow of gas, such as slow combustion.

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## A Laboratory Lifting Device

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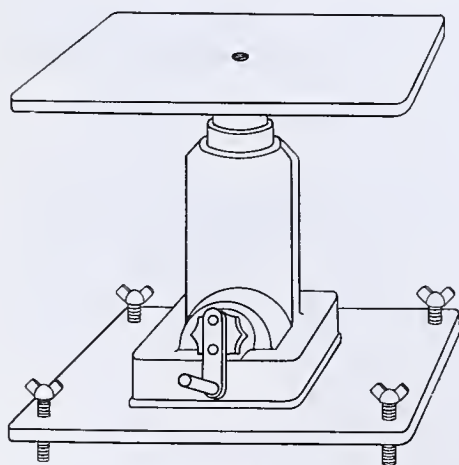


FIGURE 1

MANY operations in the laboratory call for the lowering and raising of a heating bath, such as an oil bath under a reaction flask or a still. This operation is normally accompanied by a decided hazard on account of the difficulty of handling a container of hot oil, especially when it must be

done quickly to prevent a reaction from getting out of control. A very simple device for doing this, which has been used in this laboratory for several years, is illustrated in Figure 1.

It consists of an automobile jack mounted on a plate equipped with leveling screws which are long enough to enable the plate to clear the base of a ring stand. The jack is equipped on top with a plate approximately 20 × 20 cm. which is made to support the oil bath, with or without a hot plate, or any other piece of equipment. Several makes and designs of automobile jacks have been tried out. The hydraulic type is unsatisfactory because it will not come down readily except with a large load, and also because raising and lowering require two different kinds of lever operation. The ratchet type is also unsatisfactory because an up-and-down lever operation might result in either raising or lowering, depending on the setting of the trip control lever.

The preferred type is that calling for a rotary motion clockwise for raising and counterclockwise for lowering. The dreadnaught jack No. 26, 1-ton capacity, made by the Auto Specialties Manu-

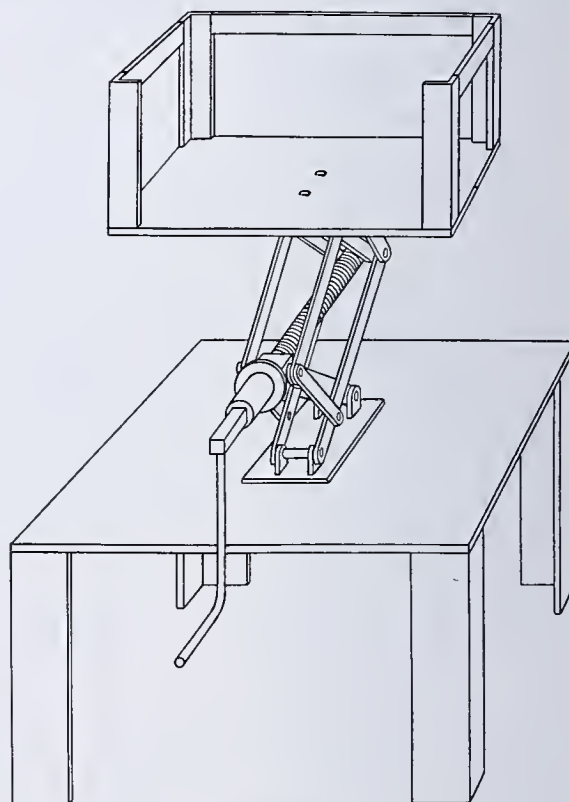


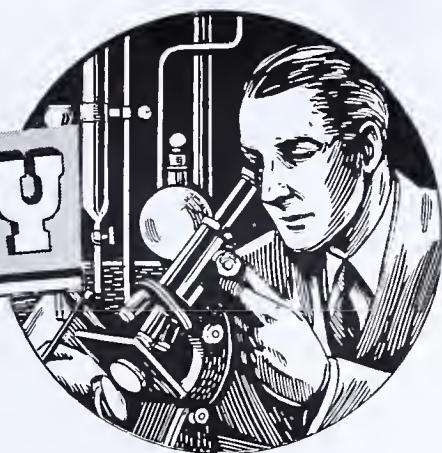
FIGURE 2

facturing Company, St. Joseph, Mich., is suitable from the standpoint of size, stability, and design and gives a total lift of 15 cm. (6 inches). It is illustrated in Figure 1. Another jack of the scissor type, illustrated in Figure 2, has a lift of 23 cm. (9 inches) but is unnecessarily bulky for general operations where the smaller jack has sufficient lift.

This type of lifting device has been found very satisfactory, not only for the repeated raising and lowering of heating baths, but also for the accurate control of heat that is required in fractional distillation.



# MICROCHEMISTRY



## Determination of Water in Paper-Insulated Cables and Insulating Oil

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THE determination of water in insulating oil, and more especially oil-impregnated paper of high-voltage cable, has received considerable attention by analysts because of its deleterious effect when present in insulating material. The procedures which have been used in the past may be divided into two main classes: gas evolution and water evolution. The former group comprises reagents such as sodium, yielding hydrogen (7); calcium carbide, yielding acetylene (1); sodamide, giving ammonia; and Grignard reagents—for example, methyl magnesium halide—producing methane (8).

In the second group the water is removed in such a manner that it is possible to ascertain its weight or volume. This is done by evacuating at room temperature and retaining the water in a low-temperature trap (solid carbon dioxide or liquid air); heating the sample to 110° to 150° C. in a current of nitrogen, absorbing the evolved material in phosphorus pentoxide, Dehydrite, or calcium chloride (2, 13, 14); refluxing with high-boiling hydrocarbon (3, 16), and centrifuging (15). The use of the quartz fiber balance for unimpregnated paper has been employed successfully by some investigators (11, 17). Critical solution in aniline (19) and heat of

hydration (10) have been used, together with many modifications of the above procedures (6). Electrical methods are inherently unsatisfactory for the determination of water.

The general criticism which may be directed at the first group of procedures is that the reagent combines with other constituents in the sample. The Grignard reagent, for example, may evolve methane by reaction with alcohols, acids, peroxides, and some hydrocarbons and, until a correction be applied to the result, the percentage of water so obtained is in error. A correction is obtained with some uncertainty for acids (5) but the other interfering substances are extremely difficult to determine in small amounts. Removal of the water by heat or evacuation, as called for in the second procedure, is almost impossible to accomplish without at the same time carrying along an impurity which would cause one to doubt the actual weight of water obtained by absorption. When the sample contains cellulose, the problem of total elimination of water presents itself, making it necessary to decide between water of absorption (free, 18), and water of composition (bound). The manner in which some of the difficulties of the second procedure are treated experimentally is described in the present paper. The apparatus is pri-

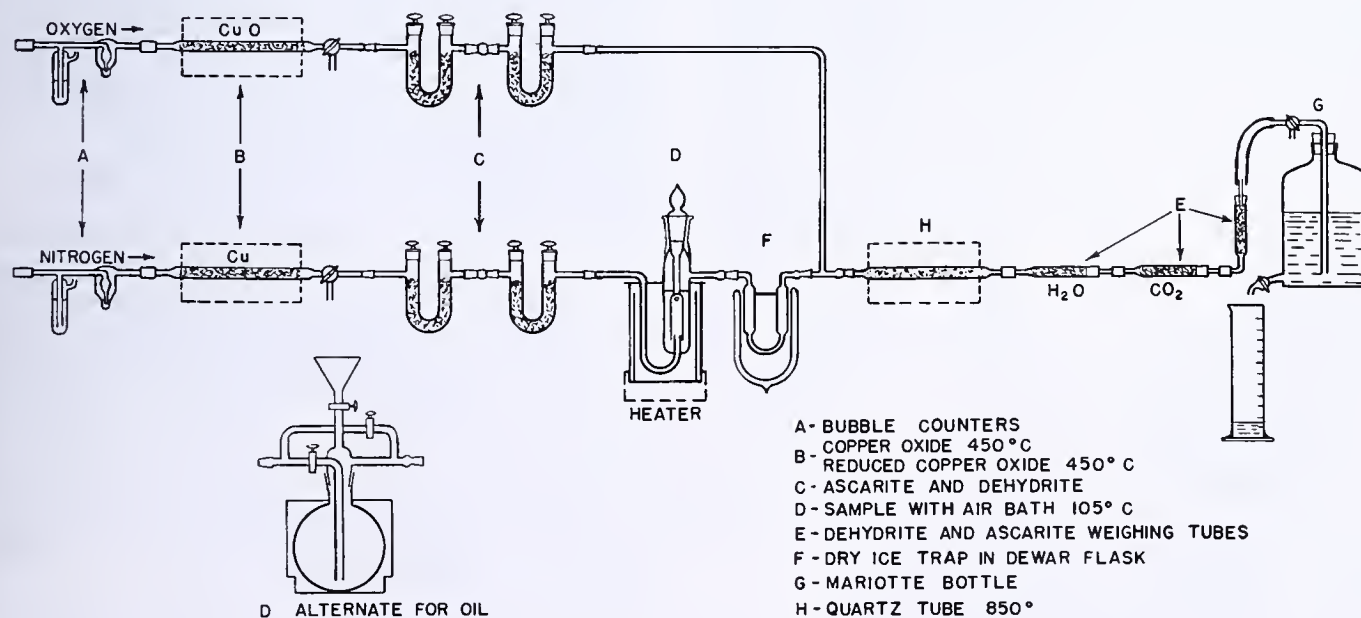


FIGURE 1. DIAGRAM OF APPARATUS FOR THE DETERMINATION OF WATER



marily applicable to impregnated paper tape, but where a somewhat larger oil sample is available a slight modification makes it suitable for analysis of water in oil.

In Figure 1, the apparatus for the determination of water is diagrammatically shown. The bubble counters, *A*, enable one to observe a constant gas velocity in the separate gas streams. The actual volume of gas is measured at the exit end of the train by the Mariotte bottle, *G*. This value determines the time of the experiment. The purification of the nitrogen is accomplished by passing the gas over reduced copper oxide at 450° C., *B*, and thence over Ascarite and Dehydrite, *C*. The same furnace serves to remove the combustibles from the oxygen in its passage over copper oxide. Cell *D* is designed for the determination of water in impregnated paper tape.

The perforated cylinder sealed to the ground-glass stopper serves as a receptacle for the sample. A minimum of handling of the sample is accomplished by merely poking the paper tape into the cylinder, cutting the ends which were handled, weighing, and immersing in the heated oil as the stopper is put in place. The oil in which the sample is immersed is the type that is used in diffusion pumps such as *n*-butyl phthalate or Apiezon oil. The latter is practically nonvolatile and is maintained at a temperature of 105° to 110° C. The quartz tube at *H* is filled with quartz fragments and held at a temperature of 800° to 850° C. The microchemical absorption tubes at *E* were prepared, weighed, and handled as discussed by Pregl (12) and Niederl (9). The cold trap, *F*, retains the expelled water and other condensable constituents but allows the passage of any hydrogen, methane, carbon monoxide, and other carbonaceous substances which if present would render the carbon dioxide correction extremely uncertain.

The general scheme of analysis is apparent from the description of the apparatus. The novel points are the immersion of the sample in hot oil, thus ensuring good thermal contact with rapid evolution of water, and the application of a correction for the volatile hydrocarbon constituents obtained by burning them and calculating the water correction from the carbon dioxide weight (4). The general formula  $C_nH_{2n}$  is arbitrarily chosen as representing the evolved carbonaceous material and thus for every milligram of carbon dioxide found, 0.4 mg. is subtracted from the weight of the evolved water. This correction was generally not large—0.5 mg. of water or less—and should represent not more than the equivalent of 5 to 10 per cent of the total water evolved. When comparatively large amounts of carbon dioxide are encountered, the method suffers in accuracy, but it is evident that the result would be more uncertain when the possibility of the absorption of hydrocarbon by the Dehydrite is considered if the expedient were not taken. In Table I, the experimental results are given in which the percentage of water for a 3-liter gas flow is listed as calculated from a ratio of 0.4 and 0.6. No great difference in the numerical result is observed, while at the same time one is assured that increase in weight of the Dehydrite tube is due solely to water. In these experiments,

TABLE I. PERCENTAGE OF WATER IN CABLE PAPER

Sample	H <sub>2</sub> O		H <sub>2</sub> O	
	Minus Blank <sup>a</sup> Mg.	CO <sub>2</sub> Minus Blank <sup>b</sup> Mg.	ratio, 0.4 %	ratio, 0.6 %
H <sub>2</sub> O. 9.8 mg.	9.95	0.00	..	..
Unimpregnated cable paper (30 days' exposure to 50% humidity)	30.40	0.05	6.46	6.46
Impregnated paper (5 min- utes exposure to 50% humidity) <sup>c</sup>	0.75	0.40	0.09	0.08
Impregnated paper (24 hours exposure to 50% humidity) <sup>c</sup>	11.00	0.30	1.57	1.55
1936—solid, CO <sub>2</sub> -purged, 27- kv. cable	1.50	0.50	0.17	0.15
1923—solid, 27-kv. cable	2.70	0.90	0.36	0.33

<sup>a</sup> Av. 0.03 mg. per liter of N<sub>2</sub>.

<sup>b</sup> Av. 0.05 mg. per liter of N<sub>2</sub>.

<sup>c</sup> Cable paper and oil were dried separately under a vacuum at 100° C. and the paper was impregnated before breaking vacuum.

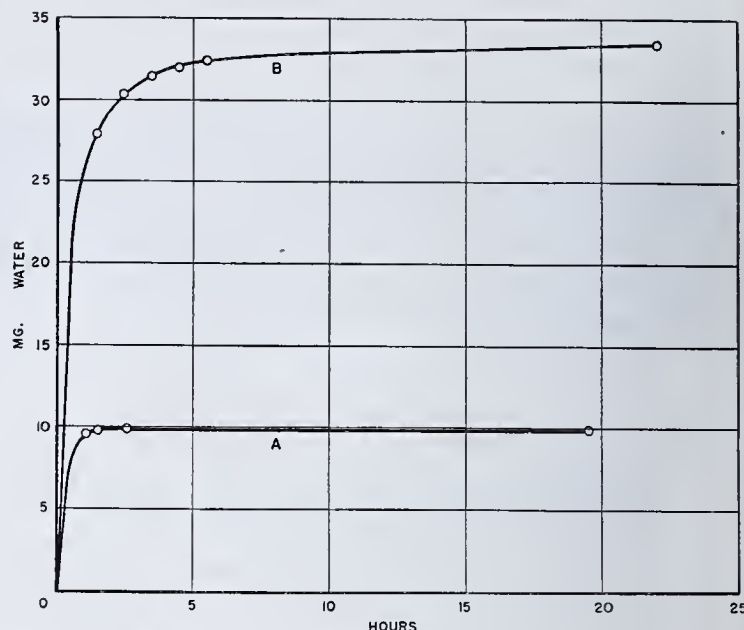


FIGURE 2. RATE OF REMOVAL OF WATER

A. 9.8 mg. of water

B. 470 mg. of unimpregnated cable paper previously exposed to air of 50 per cent relative humidity for 1 month

it was previously established that no difference in the experimental results was obtained whether or not the cold trap was used.

One of the chief drawbacks with all methods for the determination of water in cellulose products is the difficulty of removal of the last trace of water from the sample. If one wishes to avoid an arbitrary time limit to distinguish between free and bound water, it is possible to follow the time-water evolved curve and stop the experiment when it is in-

TABLE II. DETERMINATION OF WATER IN PYRANOL

	Nitrogen Liters	H <sub>2</sub> O Mg	CO <sub>2</sub> Mg.	Ratio
Blank	1	0.06	0.02	...
Trap in place	3			
Trap removed	2	11.19	7.74	1.45
	1 additional	0.47	3.52	0.116 <sup>a</sup>
	1 additional	0.52	3.30	0.130
	Gross	12.18	14.56	...
	Less blank	11.94	14.48	...
	CO <sub>2</sub> correction	1.48	...	...
	Net water	10.46	...	...
	Water, % <sup>b</sup>	0.0035	...	...
Trap in place	15	...	...	...
Trap removed	2	5.86	38.04 <sup>c</sup>	0.154
	1 additional	2.53	18.18	0.140

<sup>a</sup> 0.05 mg. less water would have produced the theoretical ratio.

<sup>b</sup> 0.0008% should be added to this percentage of water as calculated from the 15-hour heating period. However, in no case was the original blank (0.06 mg.) during the heating period subtracted. If this represents free water which would be trapped in the cold trap the 0.0008% would be considerably reduced.

<sup>c</sup> This value is approximately 5 times the value obtained in the first 2 liters of nitrogen after the initial 3-hour heating period.

indicated that the rate of evolution of water is comparatively low. In the present apparatus, 2-hour immersion was usually adequate and weighings (two pairs of absorption tubes) were taken at the end of 1, 1.5, and 2 hours. In Figure 2, the evolution of water from a sample of cable paper is illustrated. The return of 9.8 mg. of water weighed in a small capillary is also included. The weighings were carried out on the highest precision macro- and microbalances manufactured by Wm. Ainsworth & Sons, Inc., Denver, Colo. The weights of the absorption tubes could be duplicated to within 0.05 mg. on the macrobalance and considerably below this figure on the microbalance.

Where large samples (300 grams) of insulating oil are available, the alternate cell (*D*, Figure 1) may be used. Several samples of



Pyranol—a noninflammable transformer oil—were analyzed for water content, the results ranging from 0.002 to 0.004 per cent of water by weight. In these experiments the cold trap, solid carbon dioxide and methanol, was employed. The Pyranol, maintained at a temperature of 105° C. for 3 hours, was freed of water by passage of the purified nitrogen. The water and Pyranol vapors were retained by the cold trap. The trap was now removed, the Pyranol cell was isolated by means of the by-pass, and the water and Pyranol vapors were carried into the combustion furnace where combustion took place. The halogen was retained in the furnace by means of silver wool and from the ratio of water to carbon dioxide established on dry Pyranol, the net water may be readily computed.

The ratio  $C_{2n}H_nCl_n$  (aromatic) is desired by the manufacturer in order that the hydrogen and chlorine may be present in equivalent amounts. The ratio  $H_n/C_{2n}$  in terms of water and carbon dioxide equals 0.102. This value was never reached in actual experiment, as is shown in Table II.

### Advantages of Method

The procedure enables one to determine water per se without the possibility of contamination of the absorbent.

The net water may be calculated by means of a correction based on the ratio of water to carbon dioxide.

The extent of the removal of water from the sample may be judged by periodic weighings.

The determination of water is as rapid as is commensurable with accuracy.

### Acknowledgment

The authors wish to express their appreciation of the interest taken in this work by W. F. Davidson, Director of Research.

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## Microscopic Identification of Sugars

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THIS study was undertaken because there is no exclusively characteristic test for glucose and some other sugars (7). Refractive indices and certain other optical properties have been used to identify sugars (22, 42, 43), but the determination of these constants is time-consuming. The crystal habit of a few sugars has also been used for purposes of identification (8, 24, 26, 32) and it is desirable to extend this use of the crystal habit to the whole group. Microscopic fields containing sugar crystals can easily be compared for identity with the photomicrographs presented here ( $\times 80$ ).

Since the habit of a crystal is affected by the conditions of its formation (9, 12, 17, 18, 20, 21, 33, 39), a prescribed method of crystallization is necessary for useful comparisons.

Wernicke (41) and Hudson and Yanovsky (19) have successfully crystallized sugars from water solutions by addition of acetic acid or alcohol. This paper recites the use of alcohol, acetone, acetonitrile, and 1,4-dioxane in obtaining photomicrographs showing a distinctive crystal habit for each of eighteen sugars in one or more of these solvents.

### Method

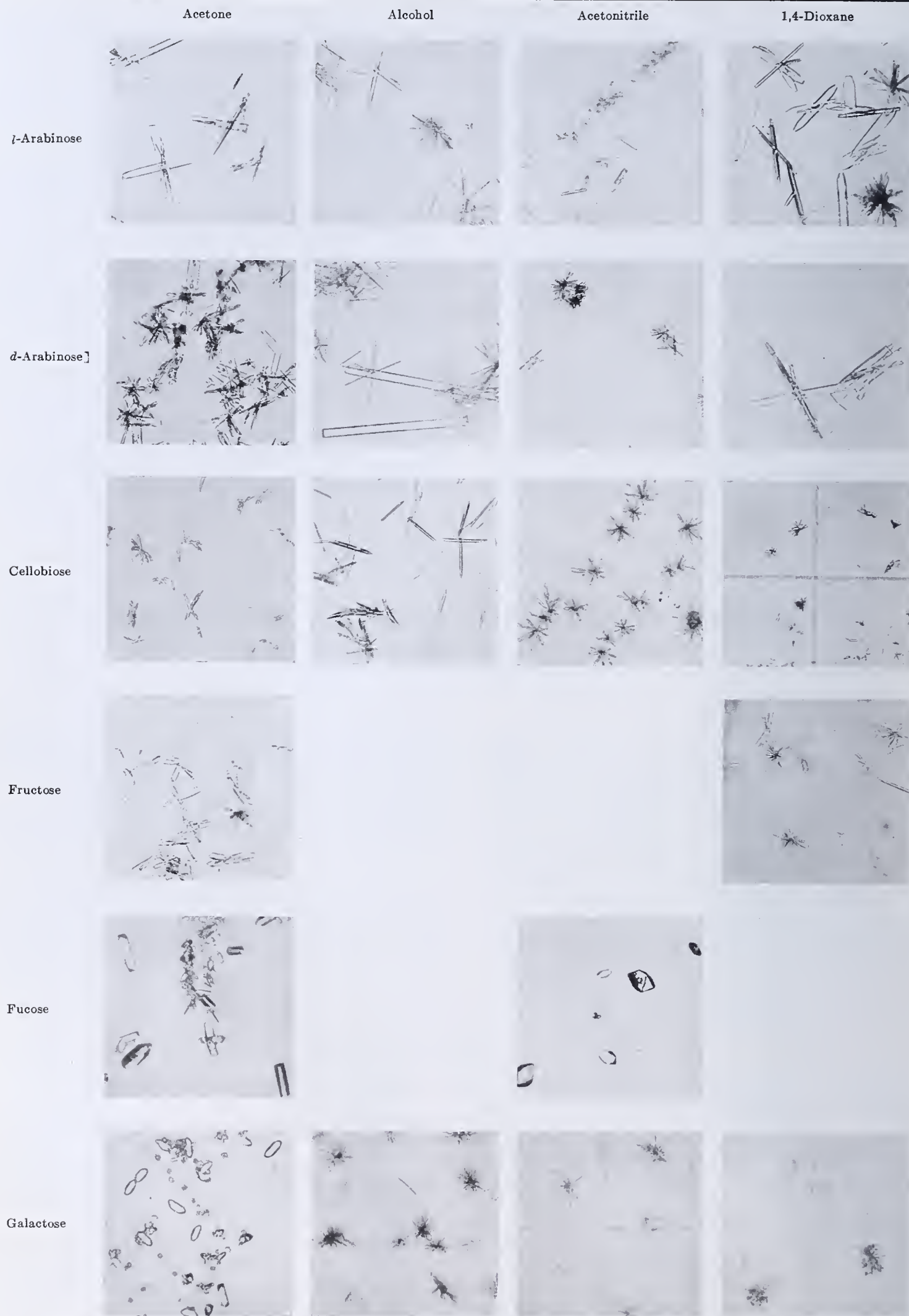
A few drops of a saturated aqueous solution of the unknown sugar in a small vial are treated with sufficient acetone, alcohol, acetonitrile, or 1,4-dioxane to cause crystallization. If the precipitating liquids are not added too rapidly, the sugar solutions usually become opalescent before crystalliza-

TABLE I. OPTICAL PROPERTIES OF SUGARS

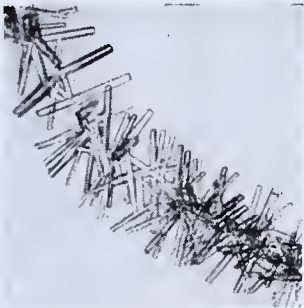
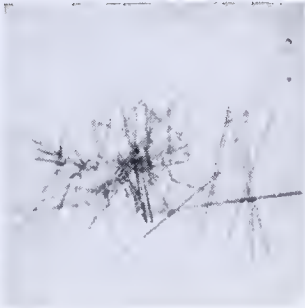
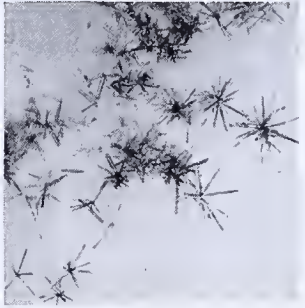
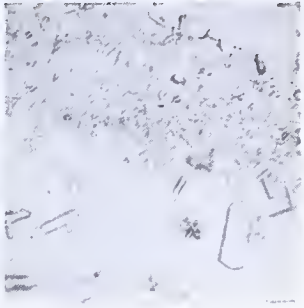
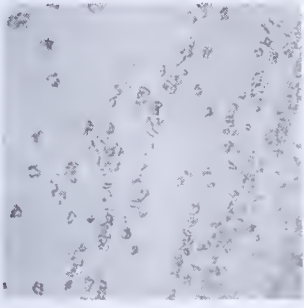
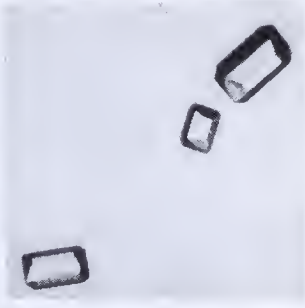

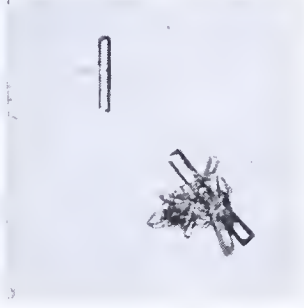
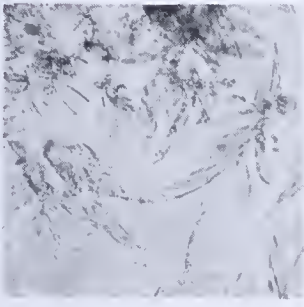

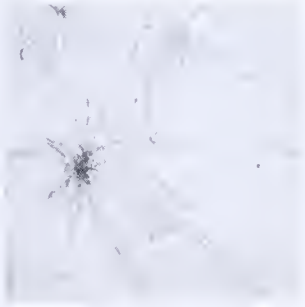

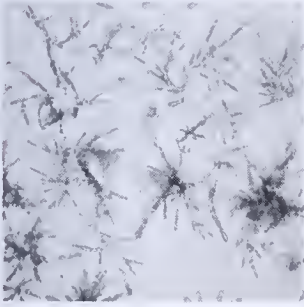
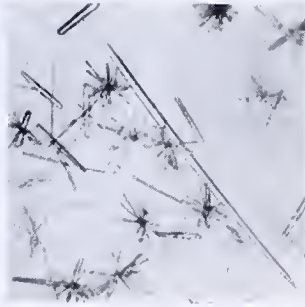

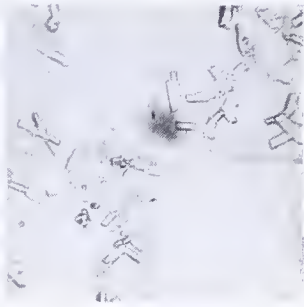
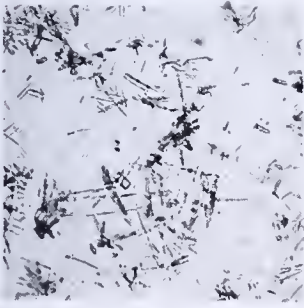
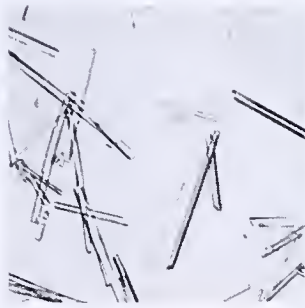
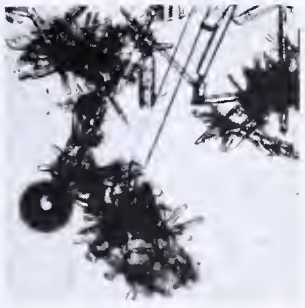

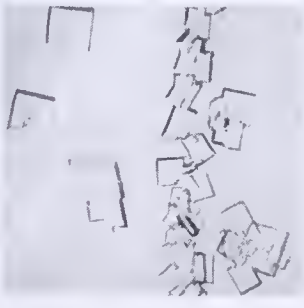


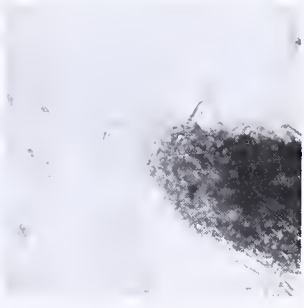
Sugar	Crystal System	Elongation	Extinction	Interference Colors
<i>l</i> -Arabinose	Orthorhombic bisphenoidal (5, 14, 30, 42)	— (22)	Parallel to slightly inclined (42)	1st and 2nd order (22, 42)
<i>d</i> -Arabinose	Orthorhombic (37)	—	Parallel (42)	2nd order (42)
Cellobiose	Monoclinic sphenoidal (16)	—	Approximately 16°	Low 1st order
Fructose	Orthorhombic bisphenoidal (16, 34)	— (22)	Parallel (22)	Low 1st order (22)
Fucose	Orthorhombic (6)	—	Parallel and approximately 25°	1st and 2nd order
Galactose	Orthorhombic (6, 23)	—	Parallel	Low 1st order
$\alpha$ - <i>d</i> -Glucose	Orthorhombic bisphenoidal (2, 4, 16, 35)	—	Parallel	1st and 2nd order
$\beta$ -Glucose	No data (35)	—	Parallel	2nd and 3rd order
$\alpha$ - <i>d</i> -Lactose	Monoclinic sphenoidal (36, 38)	—	Parallel	Low 1st order
$\beta$ -Lactose	Monoclinic sphenoidal (43)	—	Approximately 10°	1st and 2nd order (43)
Maltose	No data	—	Parallel to slightly inclined	Low 1st order
<i>d</i> -Mannose	Orthorhombic bisphenoidal (27, 28)	±	Parallel to slightly inclined (22)	1st and 2nd order
Melibiose	Monoclinic (31)	— (22)	Parallel (22)	1st and 2nd order
Raffinose	Orthorhombic bisphenoidal (13)	— (22)	Parallel (22)	Low 1st order
<i>l</i> -Rhamnose	Monoclinic sphenoidal (10, 11, 30, 36)	+	Parallel	Low 1st order
<i>l</i> -Sorbitose	Orthorhombic bisphenoidal (3, 25)	+	Parallel	Low 1st order
Sucrose	Monoclinic sphenoidal (15, 44)	+	Parallel and approximately 22.5°	2nd and 3rd order (22)
Xylose <sup>a</sup>	Orthorhombic bisphenoidal (5, 30)	+	Approximately 6° (42)	2nd and 3rd order (22, 42)

<sup>a</sup> Wherry (42) and Pionchon (29) designate xylose as monoclinic sphenoidal. The x-ray data (5, 30) were considered more reliable (1).

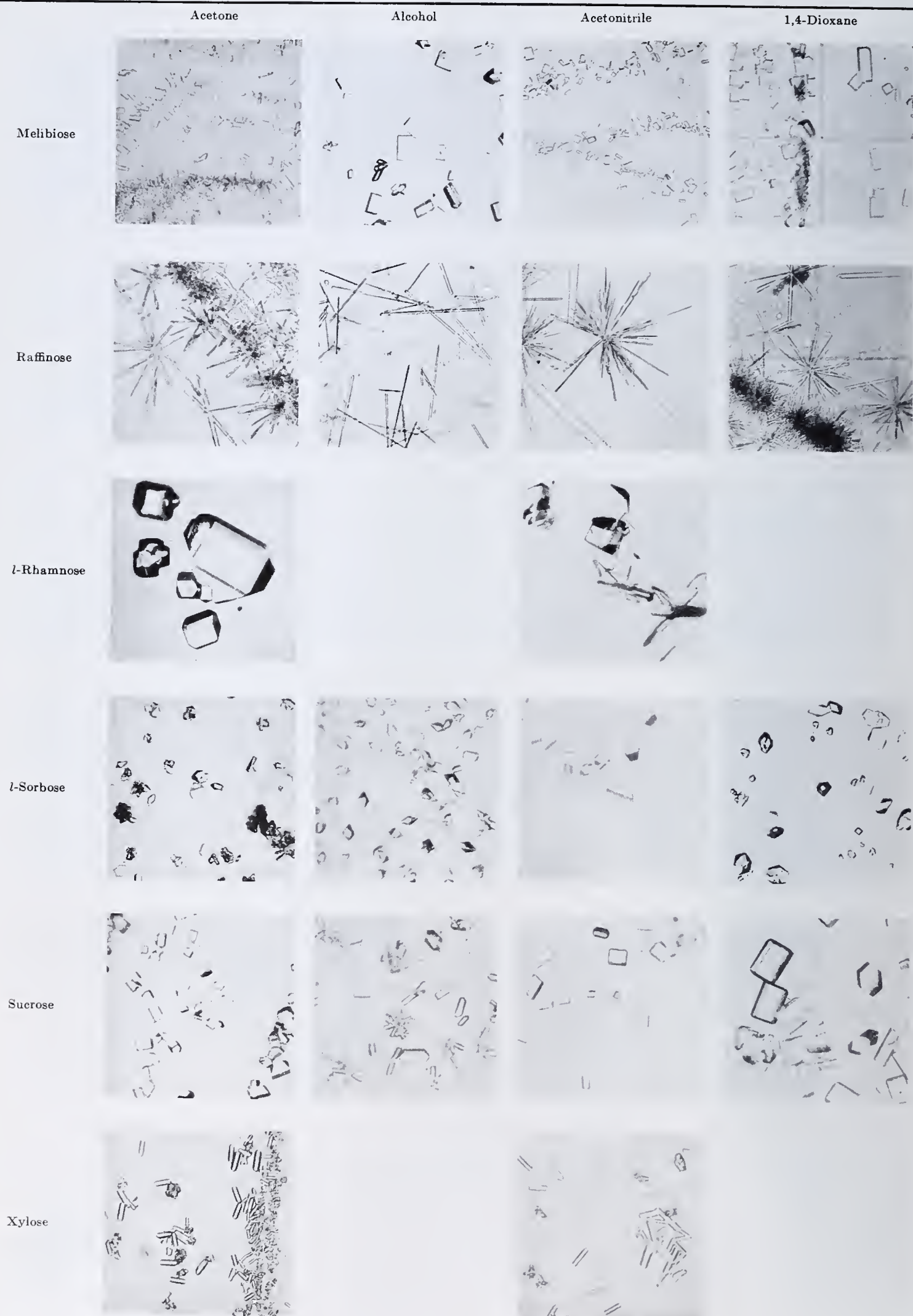






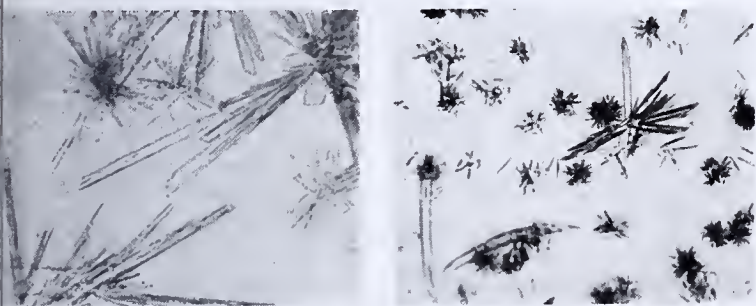
	Acetone	Alcohol	Acetonitrile	1,4-Dioxane
$\alpha$ -D-Glucose				
$\beta$ -Glucose				
$\alpha$ -D-Lactose				
$\beta$ -Lactose				
Maltose				
D-Mannose				







tion (17, 40). When these opalescent liquids are observed under the microscope, the crystals can be studied during growth. Varying speeds of crystallization and the formation of colloidal suspensions may render such observation impossible. If immediate crystallization does not occur, insufficient sugar has been used and another trial may be necessary. Should a sirup precipitate, crystallization can frequently be effected by scratching the slide (8). Comparison of a representative field with the photomicrographs leads to positive identification of the sugar. (This method has been used by graduate students on single sugars and binary mixtures with complete success.) Further confirmation can be made by study of the optical properties in Table I.



A  
B  
SUGAR MIXTURES PRECIPITATED WITH ACETONE

A. Raffinose-d-Lactose  
B. Galactose-Cellobiose

The feasibility of identifying sugars in mixtures is demonstrated in the photomicrographs of raffinose and lactose and of galactose and cellobiose. Further study of mixtures will be made.

### Remarks

In the application of this method, certain impure commercial samples failed to crystallize under any circumstances because, in the transition from the dissolved to the crystalline sugar, the impurities stabilized the colloidal stage.

Bacteriological culture slides are convenient for observations; however, the vials themselves are usually adequate. In general, acetone is the most useful precipitating liquid.

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## A Distillation Capillary

ALEXANDER O. GETTLER

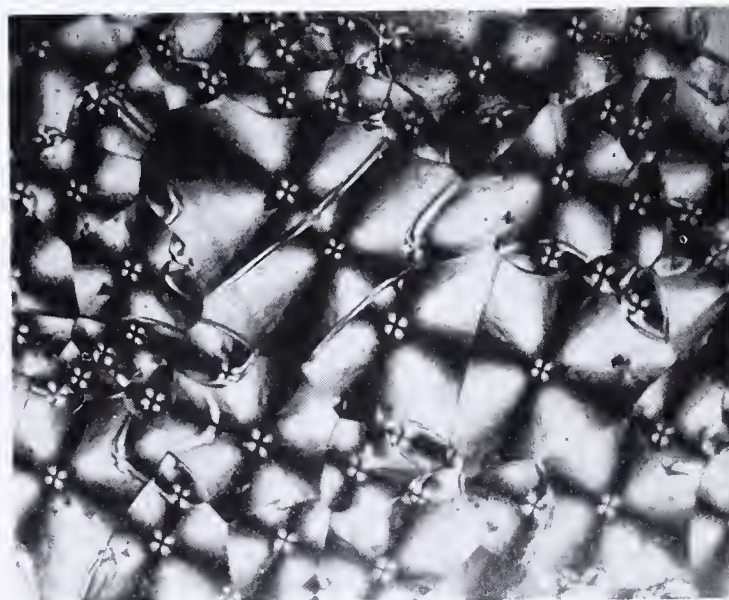
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New York, N. Y.

IN USING the distillation capillary described by Gettler and Fine (1) for the fractional distillation of 0.02 to 0.06 ml. of liquid, it was found that occasionally, as in macro-distillations, a sudden violent ebullition throws the contents of the distilling bulb up into the stem of the apparatus. This tendency has been overcome by introducing asbestos fibers into the bulb of the apparatus.

The distillation capillary is made as described by Gettler and Fine; but before attempting to form the bulb, a small quantity of previously ignited and then cooled asbestos fibers is loosely inserted into the larger capillary to a distance of about 1 cm. from the end. The bulb is then made as described by Gettler and Fine. When the distillation capillary is completed, the asbestos in the stem is forced into the bulb by simple tapping.

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Courtesy, Mary L. Willard

LIQUID CRYSTALS OF CHOLESTERYL ACETATE



# Preparation of Immersion Liquids

For the Range  $n_D = 1.411$  to  $1.785$

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ONE of the most important techniques for the rapid identification of nonopaque minerals is the determination of their index of refraction. This is done by immersing fragments of the unknown mineral in a liquid of known index of refraction and comparing the indices of the two by the standard techniques—central and oblique illumination tests with a petrographic microscope. The immersion technique is becoming increasingly familiar to chemists because an unknown nonopaque substance, inorganic or organic, may be uniquely identified in a fraction of the time necessary for a quantitative analysis.

The methods used are described in many standard texts—e. g., Winchell (13), Rogers and Kerr (11), and Chamot and Mason (5). The chemist will be especially interested in the last-named, since these men are leaders in the application of optical methods to chemistry. Tables of indices of refraction and other optical constants of nonopaque minerals are available (9, 14). Tables of inorganic artificial substances have been published by Winchell (15), who is preparing tables for organic substances.

The desired properties of the liquids used in a set of immersion liquids have been described by Larsen and Berman (9); the properties of ideal immersion liquids have been given by M. J. Buerger (2), who states that the index of refraction, temperature coefficient, and dispersion should be a linear function of composition. The liquids described in this paper represent an attempt to combine all these properties so far as is practical. These liquids are not in general suitable for work with organic crystals, since they are solvents for most organic compounds. [For these compounds a water solution of  $K_2HgI_4$  (Thoulet solution) has been suggested (see also 5, p. 375).]

The writers hope that the data on properties and the discussion of technique will be of use to those interested in preparing similar sets.

Winchell's tables (15) for artificial substances list 34 pages of index data; of these, only one page consists of substances below 1.400 in index, and only about five pages of these above 1.785. A set of liquids as described below, with index ranging from 1.411 to 1.785 in steps of 0.005, suffices therefore for all ordinary needs. For index ranges not covered in this paper the following will be helpful: West (12) has prepared liquids with index ranging from 1.78 to 2.06, using varying proportions of phosphorus, sulfur, and methylene iodide. Merwin (10) has prepared solid media with index ranging from 1.68 to about 2.10, containing three parts of antimony triiodide, one part of arsenic triiodide, and varying proportions of piperine. Barth (1) has described the preparation of mixed crystals of thallium iodide and thallium bromide with index ranging from 2.4 to 2.8. Harrington and Buerger (8) have used petroleum distillates for indices ranging from 1.35 to 1.46.

## Previous Work

A great deal has been published concerning constituents of index liquids. For many years, many liquids, each with a different basic composition, were used to prepare a set (6). This allowed no gradation in index between two end members, and the index increment between adjacent members was irregular. Additional disadvantages of this type of set are (1) irregular changes in dispersion (2), so that the evidence of color fringes in oblique illumination tests is confused; (2)

different rates of evaporation of adjacent members of the set, so that the index of an intermediate liquid changes rapidly during the measurement. These factors are not so significant in double variation work where the properties of each liquid are accurately known, but they produce serious errors in oil immersion work with white light. Thus the tendency has been to use fewer liquids (4), carefully chosen to approximate an ideal series, from which intermediate members may be prepared by mixing the end members. In this way it is possible to prepare liquids whose components have about the same rate of evaporation, and whose indices remain constant during use.

TABLE I. DATA FOR PREPARING INTERMEDIATE INDICES

$n_D$ at 22.0°	<i>n</i> -Decane Cc.	Government Oil Cc.	$n_D$ at 22.0°	<i>n</i> -Decane Cc.	Government Oil Cc.
1.411	10.00	0.00	1.445	3.80	6.20
1.415	9.26	0.74	1.450	2.90	7.10
1.420	8.36	1.64	1.455	2.00	8.00
1.425	7.44	2.56	1.460	1.09	8.91
1.430	6.53	3.47	1.465	0.19	9.81
1.435	5.62	4.38	1.466	0.00	10.00
1.440	4.71	5.29			

## End Members

The writers use the following end members to prepare liquids of intermediate index:

*n*-DECANE,  $CH_3(CH_2)_8CH_3$ , is very stable (?), colorless,  $n_D = 1.411$  at 22.0° C., small dispersion,  $d = 0.730$ , b. p. = 174°, low volatility. (It is supplied by the Eastman Kodak Co., Chemical Sales Division, Rochester, N. Y. *n*-Decane, catalog No. 2405, 100 grams \$15.00.  $\alpha$ -Chloronaphthalene, catalog No. 72, 1 kg. \$5.00. Methylene iodide, catalog No. 167, 100 grams \$4.50.)

MEDIUM GOVERNMENT OIL is very stable, colorless,  $n_D = 1.466$  at 22.0°,  $-dn/dt = 0.00035$ , slight dispersion (?). (Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Penna. Cost is about \$5.00 per gallon.)

$\alpha$ -CHLORONAPHTHALENE,  $C_{10}H_7Cl$ , is stable, colorless,  $n_D = 1.633$  at 22.0°,  $-dn/dt = 0.0004$ , moderate dispersion (?),  $d = 1.191$ , b. p. = 140–143°/20 mm.

METHYLENE IODIDE,  $CH_2I_2$ , has a light brown color,  $n_D = 1.739$  at 22.0°, high dispersion,  $d = 3.325$ , decomposes at 180°,  $-dn/dt = 0.00070$ . A few small pieces of c. p. copper (which is better for this purpose than tin) should be placed in all bottles containing this liquid to prevent decomposition and discoloration; the liquid should also be shielded from light as much as possible.

TABLE II. EXPERIMENTAL DATA

$n_D$ at 22.0°	Government Oil Cc.	$\alpha$ -Chloronaphthalene Cc.	$n_D$ at 22.0°	Government Oil Cc.	$\alpha$ -Chloronaphthalene Cc.
1.466	10.00	0.00	1.555	4.67	5.33
1.470	9.75	0.25	1.560	4.37	5.63
1.475	9.46	0.54	1.565	4.07	5.93
1.480	9.16	0.84	1.570	3.77	6.23
1.485	8.86	1.14	1.575	3.48	6.52
1.490	8.56	1.44	1.580	3.17	6.83
1.495	8.26	1.74	1.585	2.88	7.12
1.500	7.96	2.04	1.590	2.58	7.42
1.505	7.66	2.34	1.595	2.28	7.72
1.510	7.36	2.64	1.600	1.98	8.02
1.515	7.06	2.94	1.605	1.68	8.32
1.520	6.76	3.24	1.610	1.38	8.62
1.525	6.46	3.54	1.615	1.08	8.92
1.530	6.16	3.84	1.620	0.78	9.22
1.535	5.86	4.14	1.625	0.48	9.52
1.540	5.56	4.44	1.630	0.18	9.82
1.545	5.27	4.73	1.633	0.00	10.00
1.550	4.97	5.03			



FIGURE 1.  
MIXING CURVES

METHYLENE IODIDE SATURATED WITH POWDERED SULFUR. The sulfur should be dissolved at room temperature and the excess sulfur filtered off, preferably with a suction device. This liquid has a light honey-yellow color whose index varies according to the degree of saturation with sulfur, and also according to the initial index of the methylene iodide. The index of solutions prepared by the writers has varied from 1.7848 to 1.7899. After the liquid is prepared a few grains of c. p. copper shot should be immediately added; it will soon turn black but will not affect the index of the liquid which remains perfectly clear for years.

### Preparation

To determine the proportions of the desired intermediate members, one can construct a graph on a suitable scale, plotting index of refraction as a function of composition by volume. The proportions necessary to make any intermediate index can be read directly from this graph. Only in the case of an ideal solution will the mixing curve be a straight line (2). When making up whole sets it is convenient to have the composition scale read in absolute volume, instead of in per cent.

Two burets, each filled with one of the end members, may be used to mix the liquids. The correct volume of each liquid can then be put directly into storage bottles to await checking. When high accuracy in the third decimal place is not required, if large volumes are prepared (about 35 cc. to each bottle) and the volumes are measured very carefully, one can be reasonably sure that the indices are correct as read from the graph, without checking them.

The end members are *n*-decane and medium government oil for the range  $n_D = 1.415$  to  $1.465$ . The mixing curve is a straight line; data (computed for a 10-cc. total volume per bottle) for preparing intermediate indices are listed in Table I.

The end members are medium government oil and  $\alpha$ -chloronaphthalene for the range  $n_D = 1.470$  to  $1.630$ . The mixing curve is a straight line; data are listed in Table II. Butler (4) gives excellent data for a similar series using kerosene fractions instead of government oil.

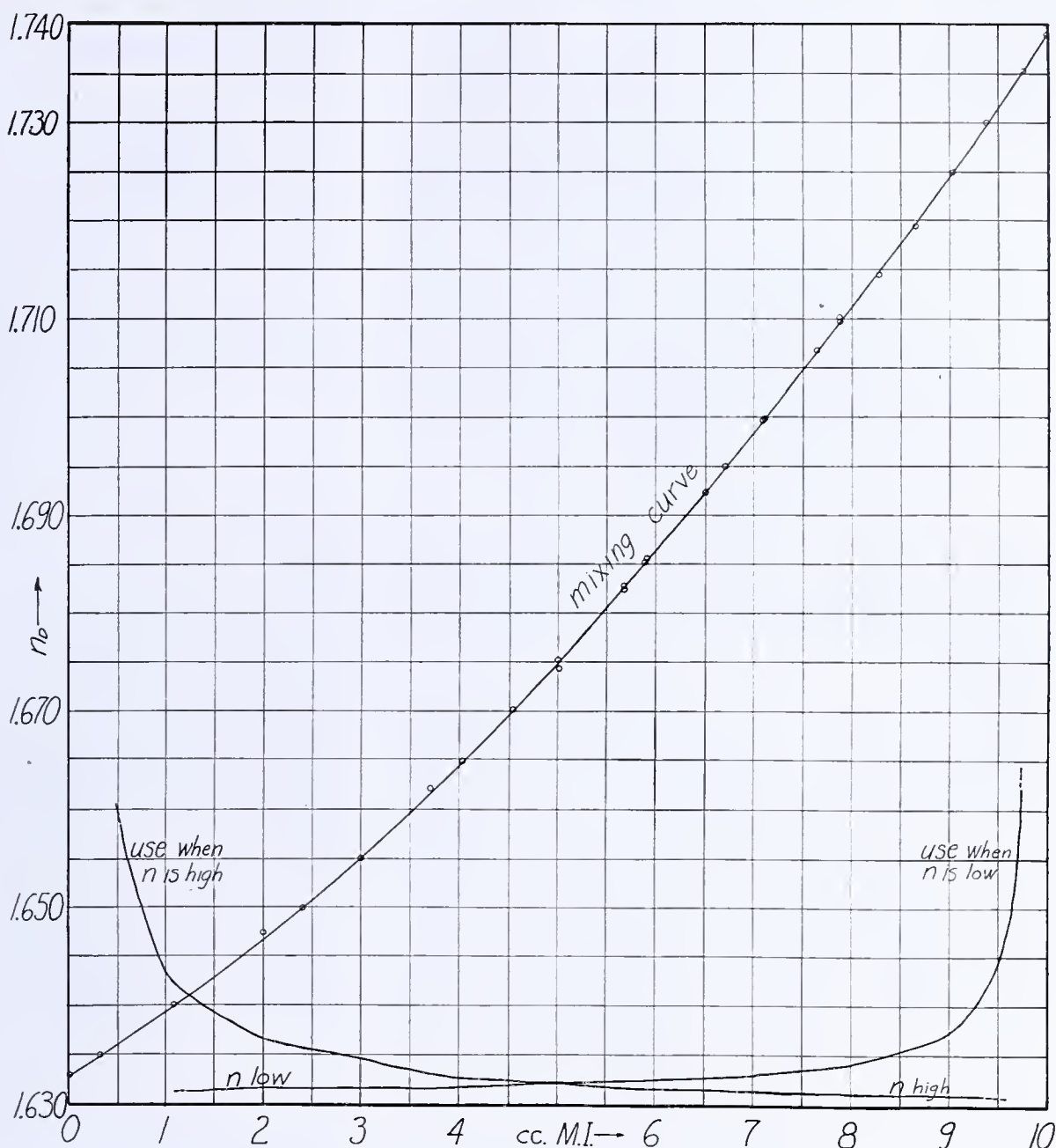


TABLE III. EXPERIMENTAL DATA

$n_D$ at 22.0°	$\alpha$ -Chloro- naphtha- lene Cc.	Meth- ylene Iodide Cc.	$n_D$ at 22.0°	$\alpha$ -Chloro- naphtha- lene Cc.	Meth- ylene Iodide Cc.
1.633	10.00	0.00	1.690	3.71	6.29
1.635	9.65	0.35	1.695	3.29	6.71
1.640	8.90	1.10	1.700	2.87	7.13
1.645	8.22	1.78	1.705	2.48	7.52
1.650	7.59	2.41	1.710	2.09	7.91
1.655	7.00	3.00	1.715	1.71	8.29
1.660	6.47	3.53	1.720	1.33	8.67
1.665	5.95	4.05	1.725	0.95	9.05
1.670	5.46	4.54	1.730	0.59	9.41
1.675	4.99	5.01	1.735	0.25	9.75
1.680	4.54	5.46	1.739	0.00	10.00
1.685	4.13	5.87			

$\alpha$ -Chloronaphthalene and methylene iodide are the end members for the range  $n_D = 1.635$  to  $1.735$ . Since the mixing curve is not a straight line (Figure 1) these liquids are not "ideal solutions" but the authors' experience has shown that they are remarkably stable and form an excellent series (3). Experimental data for this series are given in Table III.

Methylene iodide and methylene iodide plus dissolved sulfur are the end members for the range  $n_D = 1.740$  to  $1.785$ . The mixing curve is a straight line.



It is desirable to have the indices of the set graduated in steps of 0.005, and also to have the third figure after the decimal fall on 0 and 5. The mixing data in Tables I to III are for a series whose end members have the indices listed in the tables. *n*-Decane, medium government oil, and  $\alpha$ -chloronaphthalene will generally be found to have the indices listed. Different lots of methylene iodide, and of methylene iodide plus sulfur, may have different indices, however. If the index of the end member varies by more than about 0.0005 from the values listed in the tables, and if it is necessary that the third figure after the decimal be either 0 or 5, it will be found more convenient to construct a new mixing curve than use the data in the tables and make corrections. For this reason, tabulated data for the methylene iodide-methylene iodide plus sulfur series are not given; they can be easily computed for the available indices, since the mixing curve is a straight line.

### Standardization

Measurements of the refractive index are made in this laboratory at 22.0° C. in sodium light. For indices up to 1.710 the Abbé refractometer is used with white light, since correction to reading in sodium light is made with the Amici prisms on the instrument. Accuracy of this instrument is about 0.0001.

Above 1.710 a hollow prism mounted on a single-circle goniometer is employed in the minimum deviation method, a description of which may be found in any textbook of physical optics. A method of constructing a hollow prism has been described by Larsen and Berman (9). The writers used one with a 50° angle, made of plane-parallel glass plates cemented with high-temperature Picein, with a triangular piece of glass cemented between them to form a receptacle in which a few drops of liquid may be placed. Plates may be selected from object glasses by noting the reflection at a nearly grazing angle of a distant straight line, such as the edge of a building. If two images are seen the plate does not have parallel faces and is not suitable for a prism. For accurate work it is advisable to use optical flats which may be procured at slight cost. With a 50° prism and optical flats, accuracy is of the order of 0.0001, depending upon the accuracy of the goniometer circle.

Temperature may be regulated by a water bath or by working in a constant-temperature room. It is especially necessary to have a temperature control when working with methylene iodide, since its  $dn/dt$  is high.

### Corrections

The need for corrections may arise in mixing small quantities, or when old liquids are rechecked. For accurate corrections the amount to be added is calculated as follows:

We wish to prepare a liquid of index  $n_0$ , whose proportions of end members *A* (low) and *B* (high) are  $x/y$ , and we have a liquid whose index  $n_h$  is too high, with proportions (which may be read from the mixing curve) of  $x_1/y_1$ . An amount  $a$  of the low end member *A* must be added to this liquid to bring it to  $n_0$ , so that  $\frac{x_1 + a}{y_1} = \frac{x}{y}$  and  $a = \frac{xy_1 - x_1y}{y}$ . For example, if  $x/y$ , the desired proportion, is 4.5/5.5 (all proportions are on a 10-cc. basis), and  $x_1/y_1$ , the actual proportion of the incorrect liquid, is 3.5/6.5, then  $a = \frac{6.5 \times 4.5}{5.5} - 3.5 = 1.8$  cc. Thus 1.8 cc. of *A* (the low end member) are to be added to 10 cc. of the liquid of index  $n_h$  to change it to  $n_0$  (see Figure 2).

Similarly, if we have a liquid whose index  $n_l$  is too low, with proportions  $x_2/y_2$ , the high member *B* must be added in the amount  $b = \frac{x_2y - y_2x}{x}$ .

If considerable correction work is to be done, a correction curve may be drawn on the mixing curve graph.



FIGURE 2. CORRECTIONS

A certain magnitude of index difference is selected—say, 0.001—and corrections are calculated for various parts of the mixing curve. The correction curve is plotted (Figure 1) and it shows the volume of liquid to be added to prepare any desired index. One curve gives values for correcting liquids whose index is too high; the other for those whose index is too low. In using such a curve two facts must be kept in mind: (1) The calculation is based on a 10-cc. volume and must be changed by an appropriate factor if more or less liquid is to be corrected. (2) The curve has been calculated for a 0.001 index difference; if the actual difference is greater or less than 0.001,  $a$  or  $b$  will be greater or less by the same factor. The multiplying factor is not the same where the correction curve has a steep slope and in these cases each correction must be calculated. Where the curve is of moderate steepness accurate correction may be obtained for considerable index differences.

The curves have the general form  $xy = k$ . For a straight-line mixing curve, such as *n*-decane and government oil, the high and low correction curves are similar and are symmetrical about the 50 per cent composition line. Hence only one side need be calculated, and the coordinates transferred to the symmetrical position on the other side of the graph. Where the mixing curve is not a straight line, the two correction curves are asymmetric, as shown in Figure 1.

### Storage

Storage bottles should have as little air space as possible. Double air seals are not necessary if caps are kept tight. (Small square bottles of 15-cc. capacity, with glass applicators, and designed for this purpose may be obtained from the Central Scientific Co., Cambridge A, Mass. Catalog No. 66012; \$16.12 for two gross.) Each bottle should be shaken before using. The caps should never be interchanged.

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# LABORATORY EQUIPMENT

WHATEVER part one plays in the conduct of research or the application of its results to any other form of activity, there must be a realization that without adequate laboratory equipment and supplies no scientific progress would be made. Indeed, there are several instances where advances have been arrested, pending the perfection of some new laboratory device. Too often those using such equipment fail to pause long enough to remember that research along other lines was required before suitable tools became available. Here and there, however, we find one who is really interested in instruments and apparatus of all sorts. Some research men have collaborated closely with instrument makers in the design and construction of instruments used by themselves and later made available to other workers.

It is with the thought that analysts and others would like to know something of the relationships between the makers of scientific apparatus and their own work, and particularly of the lines along which research proceeds in the effort to improve instrumentation, that the following articles have been assembled for this issue. The maker of scientific equipment is more than a merchant. Many manufacturers constantly seek the advice and assistance of the users of their wares and not a few support fundamental research either in their own establishments or under their auspices in scientific institutions. In this group of papers we make but a beginning in what will become an annual feature, providing it appears to fill a need. We want to do our part in increasing the appreciation which the users of apparatus should have for the efforts of those who undertake to supply them.

## Monochromators and Auxiliary Apparatus

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BASICALLY new instruments depend on the development of new materials by chemists as well as the discovery of new properties, effects, and techniques by physicists. Tables I and II list some materials and physical effects which have been important in instrumental development in the past or from which we may expect future developments.

TABLE I. MATERIALS

Material	Properties, Uses, and Remarks
Methyl methacrylate polymers <sup>a</sup>	Not attacked by mineral oils Machines easily, does not dull cutting tools Thermoplastic, optical surfaces formed by molding Thermal expansion four times that of plate glass Electrical insulator as good as amber Very transparent <sup>b</sup> Can be cemented to form strong joints
Vinyl resins	Not attacked by mineral oils More impervious to gases than rubber, useful for vacuum hose <sup>c</sup> Aging more slowly than rubber, more inert toward ozone and ultraviolet light Not attacked by mercury Useful for enamel and insulation for electrical conductors
Low vapor pressure oils <sup>d</sup>	Substitutes for mercury in vacuum diffusion pumps; no traps needed (31) Low vapor pressure waxes useful to line steel high-vacuum vessels (27)
Kovar and Fernico alloys (3, 12, 22)	Same expansion characteristics as glass for making glass-metal seals
Alnico alloy	Strong permanent magnets
Quartz	Quartz wool-yielding filter material which does not sinter during ignitions <sup>e</sup> Quartz fibers, for suspensions in instruments (32) Reconstructed glass, yields odd shapes having low thermal expansion/ <sup>f</sup>
Glass	Fritted-glass filters Glass fabrics for filters Sealing glasses for sealing tungsten into fused quartz
Flexible Bentonite films	Inorganic parchment Mica substitute

<sup>a</sup> Lucite, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., and Plexiglas, Röhm & Haas, Philadelphia, Penna.

<sup>b</sup> Spectrum range over which methyl methacrylate resins are transparent extends farther into ultraviolet than plate glass and not so far into infrared. Transmission of a piece 0.5 cm. thick is 20% at 3000 Å. and again at 1.6 μ (19).

<sup>c</sup> Koroseal tubing, Goodrich Rubber Co., Akron, Ohio.

<sup>d</sup> Apiezon oils, manufactured in England and available through James G. Biddle & Co., Philadelphia, Penna. Synthetic organic oils, notably Octoil S, manufactured by Distillation Products, Inc., Rochester, N. Y.

<sup>e</sup> Obtainable from Owens-Illinois Glass Co., Toledo, Ohio.

<sup>f</sup> Corning Glass Works, Corning, N. Y.

New instruments will undoubtedly come from the ingenious combination of effects and materials already well known. Examples of this type of development are listed in Table III.

Finally, we have those developments which may be aptly described by the phrase "good engineering". The present article is concerned chiefly with the fundamental optical developments in astronomical and meteorological instruments with which the author is most familiar. These should be of interest to the reader because parallel developments in some chemical instruments may be expected. These developments, together with "good engineering", will increase the usefulness to chemists of all optical instruments now limited by their inadequate efficiency and sensitivity. Examples are monochromators (or spectrometers) used with either a photocell or thermopile in the visible, ultraviolet, or infrared part of the spectrum.

TABLE II. PHYSICAL EFFECTS AND TECHNIQUES

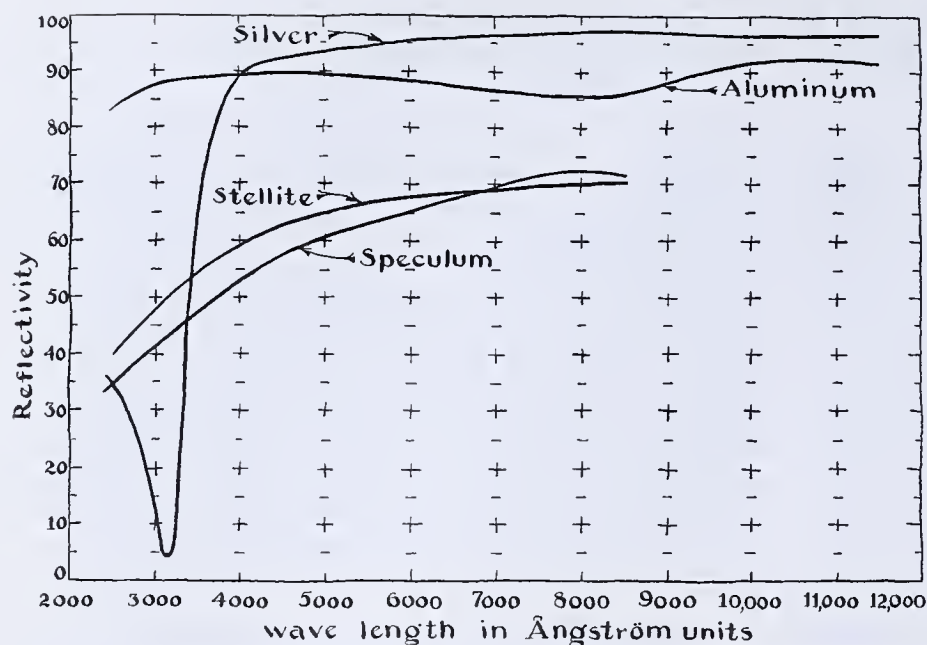
Technique	Applications
Electron optics	Improvements in electron diffraction apparatus Electron microscope Improved mass spectrograph (15, 16)
Isotopes	Enriched isotopes (example, H <sup>2</sup> ) Radioactive isotopes useful as indicators to follow course of chemical reactions
Spectroscopy (1, 24)	Infrared spectroscopy in chemistry for identification and analysis Colorimetry (18)
Vacuum technique	Low-pressure distillations for separation of hormones, vitamins, isotopes Delicate heat of reaction problems where use of high-vacuum, aluminized surfaces on containers and sensitive thermopiles will increase attainable precision

TABLE III. INSTRUMENTS

Name	Remarks
Electrometer tubes	Electronics
pH meter	Use of electronics techniques with glass electrode
Vacuum balance	Use of Alnico magnets
Packless and greaseless valves	Use of ductile brass and glass bellows <sup>a</sup>
Polaroid	Substitute for nicols (see Figure 5)
Colorimeters	Use of photovoltaic photocells
Fractionating columns	Employment of principles of Dewar flask
Super-high-pressure mercury lamp	Quartz-tungsten seals
Electric titrations	Use of electric eye

<sup>a</sup> Metallic bellows obtainable from Fulton Sylphon Co., Knoxville, Tenn., and Clifford Mfg. Co., Boston, Mass. For description of glass bellows see (2).





Credit, Prentice-Hall, Inc.

FIGURE 1. REFLECTIVITIES OF METALS USED FOR MIRRORS IN INSTRUMENTS

### Surface Films by Evaporation

Glass is used for astronomical mirrors and lenses. The reflection coefficient of a glass surface is not ideally suited for either of these applications, being too low for the former and too high for the latter. But the reflection coefficient of the surfaces of mirrors and lenses is altered by thin surface films deposited by evaporation. This increases the efficiency in both cases; a thin film of aluminum (Figure 1) gives a glass mirror a reflectivity of approximately 90 per cent throughout the entire useful spectrum (27); a thin film of calcium fluoride on the surfaces of a lens eliminates 90 per cent of the transmission losses arising at the surfaces owing to reflection (29).

These surface films have been applied to increase the efficiency of monochromators. The use of evaporated aluminum films has eliminated the expensive roof prisms used in the early models of one double-quartz monochromator (see Figure 2). The use of evaporated fluorite films on this same double monochromator will more than double its transmission. The high gain resulting from the application of fluorite films is achieved because the light beam in this monochromator penetrates twenty quartz-air surfaces.

### Double-Quartz Monochromator for Ozone and Water Determinations

The double-quartz monochromator, shown in Figure 2, is in use with the sun as a light source, to make routine analyses of the entire atmosphere for ozone and water vapor content.

For the ozone determination, which takes only 2 minutes, a sodium photocell in an evacuated quartz-glass envelope is used as a receiver. The photocell current is amplified with an electrometer tube (34). The intensity of the sunlight at 3050 Å. and 3110 Å. is measured. For the water vapor determination, which takes 5 minutes, the intensity of the  $\phi$ -band at 1.15  $\mu$  is measured with a thermopile (10). It is noteworthy that the slits of the double monochromator remain the same for both determinations (0.075 mm., 0.003 inch).

Determinations have been made of the ozone in an absorption cell using the relative absorption at 3050 Å. to 3110 Å. Here a tungsten-filament lamp in a quartz-glass envelope serves

as the source of continuous radiation. (Tungsten lamps in quartz envelopes are supplied by the Phillips Laboratory, Eindhoven, Holland.) This source is useful from 2800 Å. to 3  $\mu$ . The voltage across the filament is regulated by a Raytheon regulator, the performance of which is expressed as follows (data taken with the output power adjusted to full load):

Applied voltage	70	80	90	100
Output voltage	114	116	116.0	116.0
Applied voltage	110	120	130	150
Output voltage	116.0	116.1	116.1	116.1

With the slits 5 Å. wide the response of the galvanometer at 3050 Å. is about 100 divisions. The ratio of the emission at 3050 Å. to that at 3110 Å., for the empty cell, is reproducible to one part in 1500. With this inherent reproducibility one can get an accurate determination of the ozone in the absorption cell.

The monochromator shown in Figure 2 and its accessories have been used for measuring the reflection of mirrors, the transmission of optical glass, the absorption of filters, and the spectral response of photoelectric cells. The use of a double monochromator is required for highly selective effects like the photoelectric effect, and its use in colorimetric work is recommended when highly selective receivers are employed.

TABLE IV. INDEX OF REFRACTION OF SYNTHETIC MATERIALS

Material	C	D	e	F	g
	6563	5893	5461	4861	4358
Fused quartz	1.4567	1.4587	1.4604	1.4634	1.4669
CaF <sub>2</sub>	1.4325	1.4338	1.4349	1.4369	1.4395
LiF	1.3906	1.3922	1.3930	1.3943	1.397
KCl	1.4870	1.4901	1.4929	1.4981	1.5043
KBr	1.5544	1.5590	1.5631	1.5709	1.5806
KI	1.6569	1.6655	1.6721	1.6853	1.7025
MgO	1.7337	1.7378	1.7412	1.7475	1.7550
Plexiglas	1.4856	1.4881	1.4902	1.4938	1.4992
Lucite	1.4916	1.4945	1.4967	1.5008	1.5064

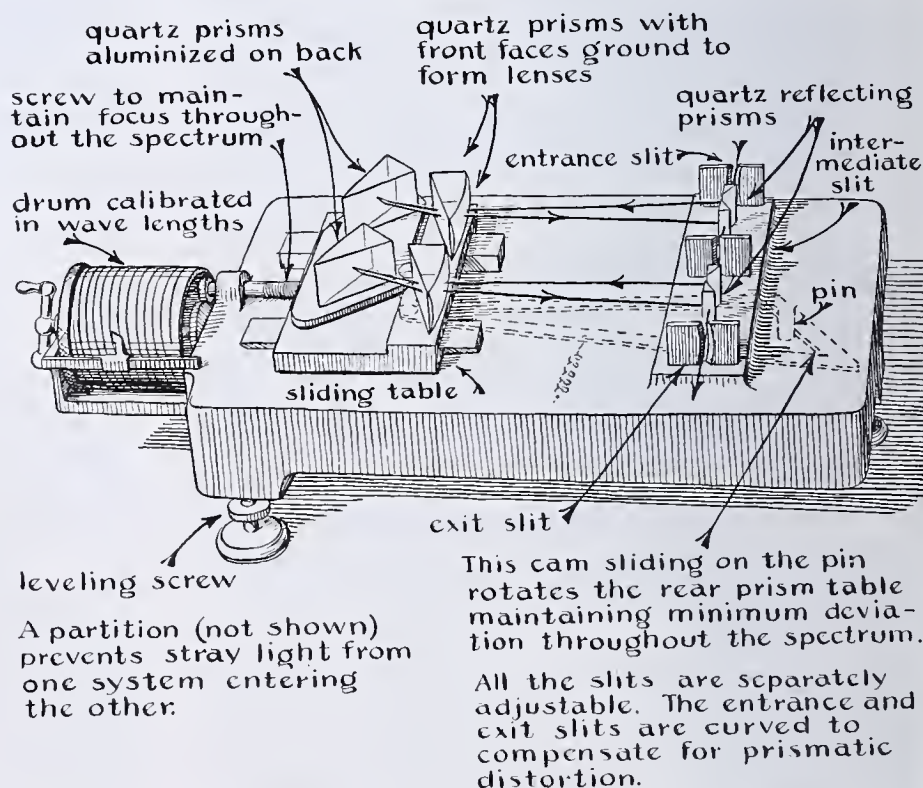


FIGURE 2. HILGER-MÜLLER DOUBLE MONOCHROMATOR WITH QUARTZ OPTICS  
Two prisms at left, shown here backed with reflecting coats of aluminum, were formerly backed with quartz roof prisms

Credit, Prentice-Hall, Inc.



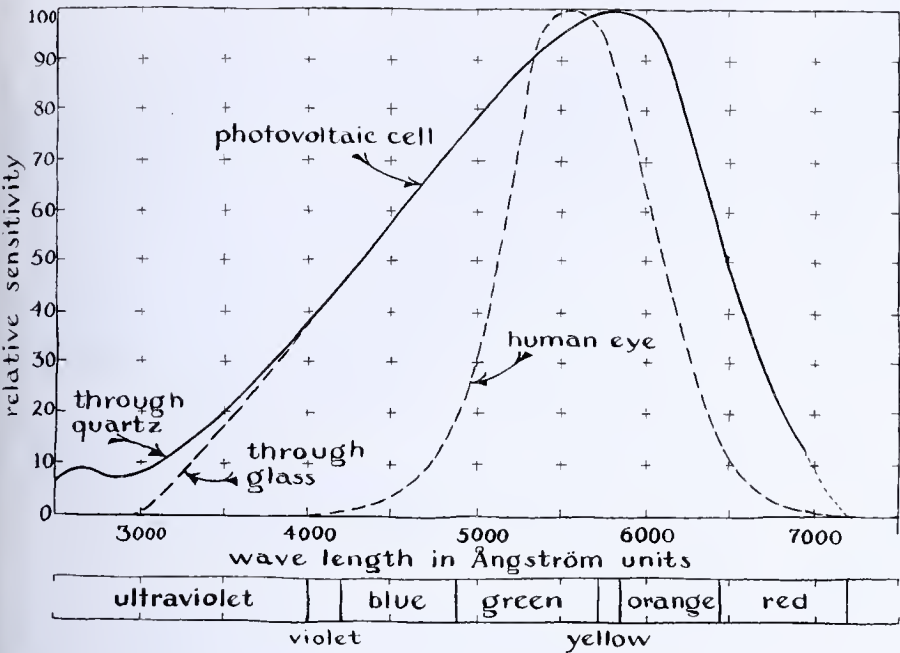


FIGURE 3. SPECTRAL SENSITIVITY OF PHOTOVOLTAIC CELL  
Note that sensitivity goes to zero on long wave length side at approximately 7200 Å.

New Optical Materials

The infrared spectrum is being used now by chemists to identify compounds and to estimate the proportions in which they are present (1).  
The growing of large synthetic crystals of the alkali halides was undertaken in order to supply prisms of new optical materials for infrared spectroscopy. Synthetic crystals of potassium chloride, potassium bromide, and potassium iodide were grown at the University of Michigan in cylinders 12.5 cm. (5 inches) in diameter by 12.5 cm. (5 inches) long (30).  
To this list have been added two synthetic crystals, sodium fluoride and lithium fluoride, which are of importance in the ultraviolet and visible part of the spectrum (25). These two materials are important (4) because they simulate the properties of fluorite (see Table IV). The occurrence of fluorite in large size and quality suitable for optical usage is now very rare.

Another synthetic optical material now available (from the Norton Company, Chippawa, Canada) is magnesium oxide, which is useful in infrared spectroscopy for making shutters. Its transmission limit in the infrared is intermediate between that of quartz and fluorite (about 7.5 μ) and in the ultraviolet is 2300 Å. Magnesium oxide has a high index of refraction and a low dispersion (see Table IV). Its inertness toward the alkali metal vapors suits it for use as a window material for absorption cells to contain these vapors (35).  
Synthetic thermoplastics (Lucite and Plexiglas) are now used for making unbreakable spectacle lenses and sun glasses and may eventually find extensive use in optical instruments (36). Their optical surfaces are formed by heat and pressure in polished molds without any of the customary optical working with abrasives and rouge.

Radiation Receiving Devices

Photocells are not treated here (they are adequately discussed elsewhere, 18) except to point out that the sensitivity of the photovoltaic type vanishes completely at about 7200 Å. (see Figure 3).  
Improvement of the sensitivity of thermopiles and other radiometric devices has been the object of many investigations (33) and work is now being done to improve their performance. There seems at present no possibility of making "order of magnitude" improvements in the sensitivity of this type of instrument, which measures a flux of radiant energy, because the delicacy of the measurements is now limited by the effects of Brownian motion. Recently, however, a novel method has appeared for photographing in the infrared spectrum out to 9 μ (5-7, 17, 37). Because, in principle, this new method integrates the flux of energy over the time of exposure, it is not inherently limited by the effect of Brownian motion and we may reasonably expect that it or some modification of it may be developed which will yield an instrument of great sensitivity.  
But without radical developments in radio-

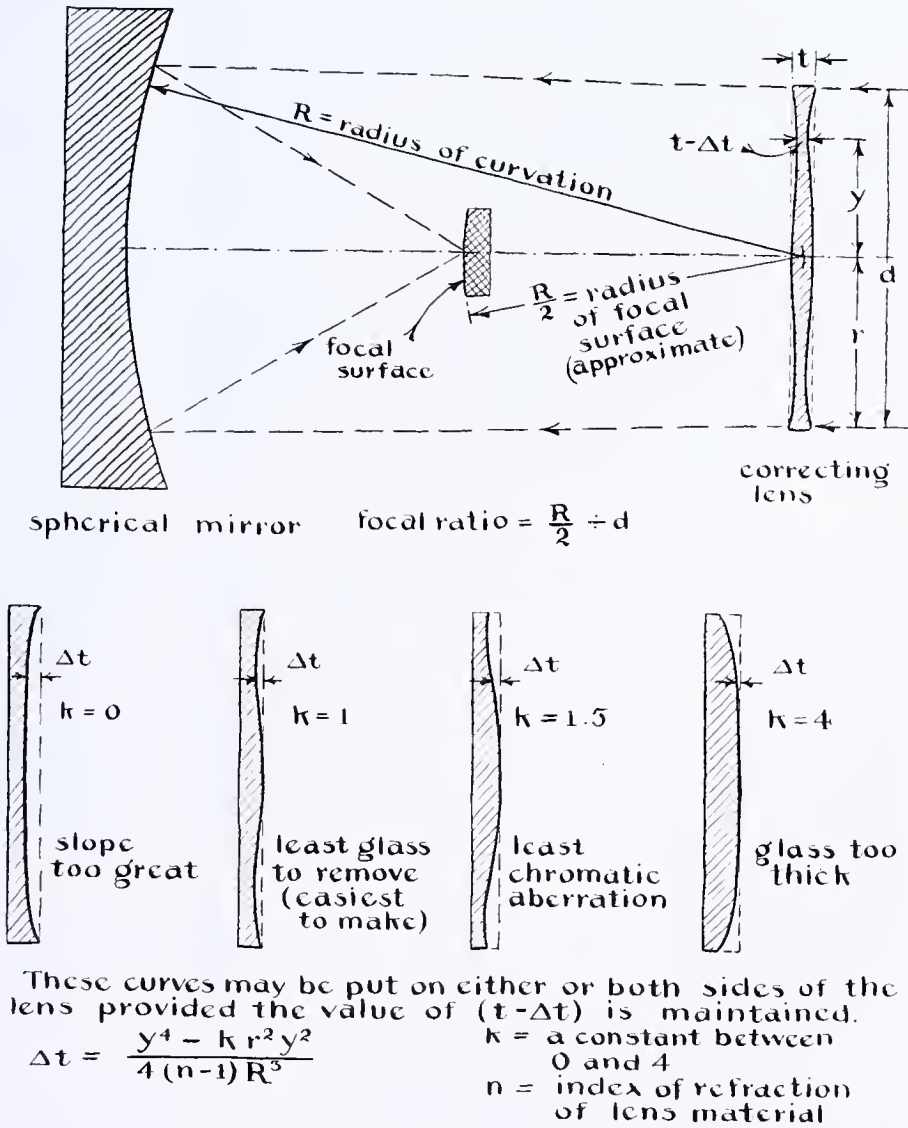


FIGURE 4. DIAGRAM OF SCHMIDT PRINCIPLE AS APPLIED TO AN ASTRONOMICAL TELESCOPE  
Above. Parallel light from the right is modified by the correcting lens so that the spherical mirror at the left focuses it to a point. Below. Various shapes that may be given the correcting lens and formula describing their contours



metric instruments we can expect definite advances in the technique of working with the instruments now available.

For example, to measure with a thermopile most effectively the energy emergent from the slit of a monochromator (especially as applied to infrared spectroscopy) it is necessary to form a reduced image of the exit slit on the thermocouple and at the same time increase the solid angle within which the thermocouple is irradiated. At present an elliptical mirror is used, giving a fivefold reduction in the image size and an increase of angle of irradiation to a cone of  $100^\circ$  diameter (9, 20). The thermopile is at one focus of the elliptical mirror and the exit slit of the monochromator is at the other focus. The elliptical mirror is not completely suited for this application, for although the image is definite on the optical axis the imaged ends of the slit which lie off the optical axis exhibit coma (8). This coma necessitates the use of an oversized thermopile receiver. The technique may be improved by applying the Schmidt principle instead of an elliptical mirror. Thus, without any sacrifice in the solid angle of irradiation, the area of the thermopile receiver may be reduced three- or fourfold with an attendant doubling of the thermopile sensitivity.

### The Schmidt Principle in Optical Design

The Schmidt principle in optical design is described in a recent issue of the *Scientific American* (11). The Schmidt principle involves the use of a lens positioned at the center of curvature of a spherical mirror (Figure 4). The lens is figured to introduce a compensating spherical aberration in a parallel beam of light, so that the spherical mirror can focus the beam to a point. As the effect of the lens is not critical in respect to the angle at which the beam passes through the correcting lens, the combination of mirror and lens exhibits a large field. The Schmidt lens introduces but very little achromatism and because it is thin it introduces but little absorption. Many applications of the Schmidt principle have been discussed (11, 23, 26).

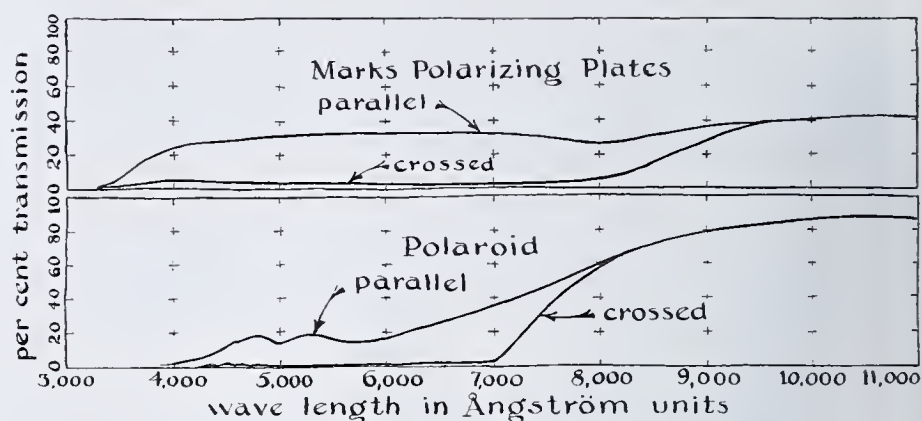
Although the making of Schmidt correcting plates is now an optical task of considerable difficulty, the principle may, in the future, be used in the construction of an inexpensive but effective double monochromator. Perhaps the Schmidt correcting plates will be formed from methyl methacrylate polymer by pressing, in the same manner that spectacle lenses are now made.

### Replica Gratings

Excellent replica gratings (both reflection and transmission types) which throw a large fraction of the incident light in a single order of the spectrum, are now available. [Replica gratings produced from matrices made by R. W. Wood are obtainable from the W. M. Welch Scientific Co., 1518 Sedgwick St., Chicago, Ill. Transmission replicas can be transformed into reflection replicas by aluminizing the cellulose film (27).] Combined with a fore-prism monochromator to eliminate overlapping orders and stray radiation, these replica gratings may be used in certain types of monochromators to obtain a linear wave-length scale and a greater dispersion than a prism affords.

### Other Applications of Nonreflecting Surface Films

Nonreflecting surface films of fluorite and other substances are deposited by evaporation on optical surfaces primarily to make optical instruments more efficient. In addition, these nonreflecting films eliminate halations and the thin veil of background light produced in a lens by internal reflections. Many applications of these films are possible, wherever surface reflections from a transparent optical body are to be eliminated. Promising among them are the application of non-reflecting surfaces of fluorite to decrease the reflectivity of residual-ray crystals in the near infrared and the application



Credit, Prentice-Hall, Inc.

FIGURE 5. CHARACTERISTICS OF HERAPATHITE POLARIZING ELEMENTS

of paraffin layers  $20\ \mu$  thick to quartz to increase the transmission of quartz lenses in the far infrared.

### Residual-Ray Filter Method in the Far Infrared

The residual-ray filter method uses successive reflections from crystals to obtain monochromatic bands of infrared radiation. The method affords, in effect, a monochromator. Wave-length bands from  $6.7\ \mu$  to  $150\ \mu$  are thus obtained (8, 14). A new arrangement of the residual-ray apparatus using a band of radiation at  $8.8\ \mu$  affords a pyrometer particularly suited for determining surface temperatures in the range  $-100^\circ$  to  $+100^\circ\text{C}$ . (28). The band of radiation used in this pyrometer as the thermometric property lies at a position in the infrared spectrum where water vapor is very transparent. Accordingly, no corrections for absorption in the optical path of the pyrometer are ordinarily required. With the pyrometer one can measure the temperature of surfaces without interfering with heat loss by radiation and convection or with surface heating.

This instrument was intended for astronomical (sun, moon, star, and planet temperatures) and meteorological (ozone, air, tree, grass, and ground surface temperatures) applications but it is possible that it will find other applications. Fitted with appropriate crystals, the residual radiation falls exactly on the ozone band lying in the infrared spectrum at  $9.6\ \mu$  and the instrument so arranged is being used daily to measure the absorption of sunlight by the ozone of the atmosphere. Using a residual-ray band at  $6.7\ \mu$  obtained with calcite crystals, there is a linear relationship between the square root of the water vapor in the optical path,  $\tau$ , expressed as centimeters of precipitable water, and the produced fractional absorption of the energy in the residual-ray band,  $A$ :

$$A = 4.4 \sqrt{\tau}$$

Thus one may determine, with the apparatus, the absolute humidity. The above relation on which this "chemical analysis" is based is valid only at ordinary temperatures and at atmospheric pressure (13, 21, 38).

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## Coordination between Instrument Maker and Research

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THE close integration that may exist between instrument maker and research laboratories is well illustrated by the experience of this company. The men who founded the organization 25 years ago were skilled technicians who had been associated exclusively with experimental groups. It was natural, therefore, that their independent activities should from the start have consisted in the construction, according to sketch or published paper, of fine instruments and equipment for governmental, educational, and industrial laboratories. Many published contributions have rested strongly on a specialized apparatus carefully constructed by this establishment.

This policy of close contact and collaboration with organized research groups, although greatly extended and varied, has remained essentially the same through the years. In a large new plant, generously equipped with standard and highly specialized tools, construction proceeds at any one time on a number of different instruments designed to fill special research needs. Scientists from governmental laboratories and from schools in the vicinity of Washington, D. C., frequently avail themselves of facilities not to be found elsewhere. The present new plant has 20,000 square feet of floor space. The organization is divided into several closely knit sections, the principal ones being the technical and development section and the fine tools division.

The rapid tempo of scientific development requires incessant scrutiny and study of the literature and contact with leading laboratories.

New instruments and new designs of old instruments find their fitting counterpart in new materials of construction, machines, and methods. Skill, resourcefulness, and economy of manufacture alone no longer suffice to meet the demands of an exacting scientific world, but the fabrication must be guided by and conform to inexorable theoretical requirements. This aspect is taken care of by the highly trained technical section, which is closely integrated with the production department. It is not unusual for the construction of an instrument and its proper employment to be conditioned by exacting mathematical relationships.

Coordination with and service to chemical and physical research laboratories are, however, hardly complete if they stop at the point of making specialized instruments. The plant and skills of the organization are therefore directed toward the manufacture of standard instruments and routine laboratory equipment. In all these operations the same type of skilled mechanic is employed as in the special instrument con-

struction. The standard apparatus is mainly for testing, for control, and for analysis, and fabrication is of metal, glass, or other material.

### Services

It may be thought that the product of an instrument company is nothing more than a home-made gadget in fancy dress. This is far from being true. Into each instrument enter desirable and indispensable values that result from much thought, planning, combined skills, and the application of special tools and methods. The product of a reputable instrument company will give more accurate, rapid, and certain measurements and results than the comparative makeshift of the hurried and unspecialized laboratory worker. A case recently came to notice of the loss of time and ruination of experimental work caused by a home-made thermoregulator. The construction seemed relatively easy, but unexpected difficulties of fouling of the mercury, breaking of the thread, etc., arose which are to be contrasted with the simplicity, reliability, and accuracy of, for example, a metastatic thermoregulator.

Besides offering substantial improvements over home-made equipment, a further type of service consists in the production of instruments and apparatus that the average shop is scarcely equipped to make. An example is the preparation of fused glass absorption cells with guaranteed plane parallel ends, which requires highly specialized skill and tools.

A third type of service consists in a more economical and efficient construction than is possible in the average laboratory, yet with at least equal accuracy. Recently the company was faced with the task of constructing a respirometer according to a published design. It was found possible after suitable consideration to prepare a very much simpler piece of equipment which functioned the same and just as effectively; the simplifications cut the cost considerably, and resulted, in fact, in putting the instrument on the general market.

A further contribution of value consists in making generally available, very shortly after publication or announcement, instruments and equipment that have obvious merit. There have been several instances in which a demand for an instrument, promptly proclaimed after publication, was just as promptly met. In this way the findings and accomplishments of research laboratories come into general use a long time, years perhaps, before they would without the service rendered by the modern instrument company.



The company has found it desirable to sustain cooperative fellowships and research undertakings in connection with instrumentation. Two such are in operation at present. The main objective of one of these has been to develop the most scientific method of use and most efficient design of an important instrument for fine size analysis, which is manufactured by the company. This fellowship has been unusually fruitful and has resulted in fundamental findings. The second research is in the automotive industry and has to do with the study of the various conditions of use of engine indicators so as to develop their widest utility.

### Costs

The undeserved penalty of good appearance is sometimes the impression that the cost has been polished up, so to speak. As far as established instrument making is concerned, this is not true, nor can it be under competitive conditions. The notion may be based on a hurried and fallacious method of accounting. One cannot estimate the cost of an instrument, any more than anything else of use value, on the basis of the value of the component materials. There are items to be

considered of initial technical investigation, experienced engineering design, and skilled machine construction, all of which lead to a more efficient, more durable, and more presentable article than in the absence of these services. One need hardly mention also the usual economic items of capital investment, obsolescence, overhead, salary, etc., which should be taken into account when an investigator attempts his own construction. Finally, one may note the saving of valuable time and effort, as far as the real objective of the investigator is concerned, when he has before him a highly satisfactory instrument, ready for use.

In conclusion, the instrument maker is interested in the problems of the investigator and research worker. In fact, he has to be, for it is only on the basis of the broadest knowledge of the requirements of the laboratory that he is able to render a fitting service. In this sense, he welcomes the inquiries and interest of the investigator, and he is prepared fully to cooperate with him.

The scientific research world has been implemented thereby in a manner that has created more accurate results and broadened research horizons beyond the fondest dreams considered possible only a few short years ago.

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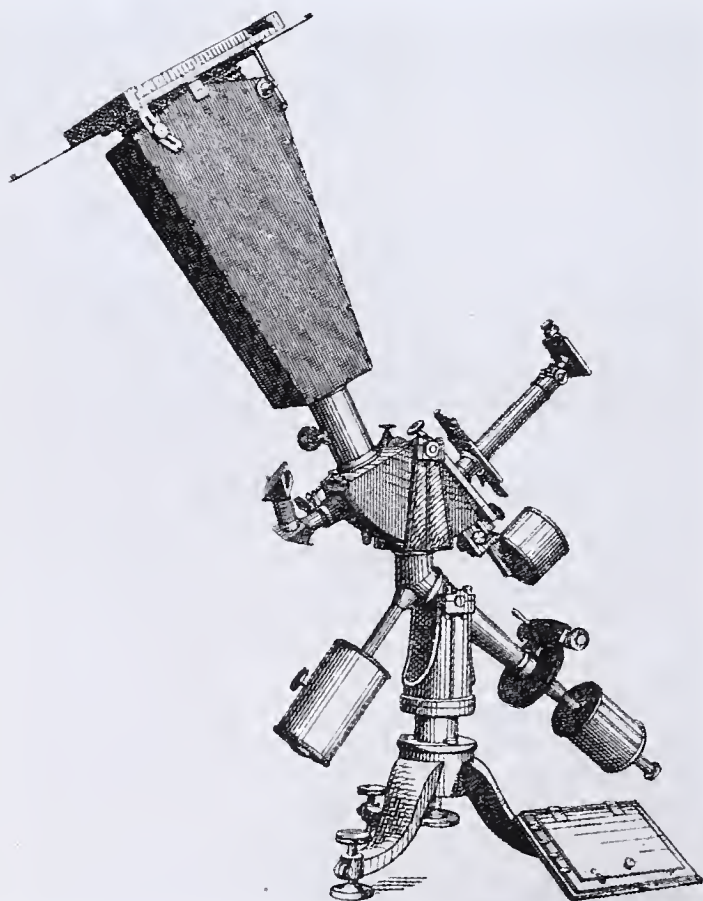
## Spectrograph Design and Its Problems

J. W. FORREST, Bausch & Lomb Optical Co., Rochester, N. Y.

OPTICAL instruments of various kinds are extremely valuable in chemical analysis. Microscopes, colorimeters, polarimeters, saccharimeters, and refractometers are extraordinarily useful tools for the identification of unknown substances or for the determination of the degree of concen-

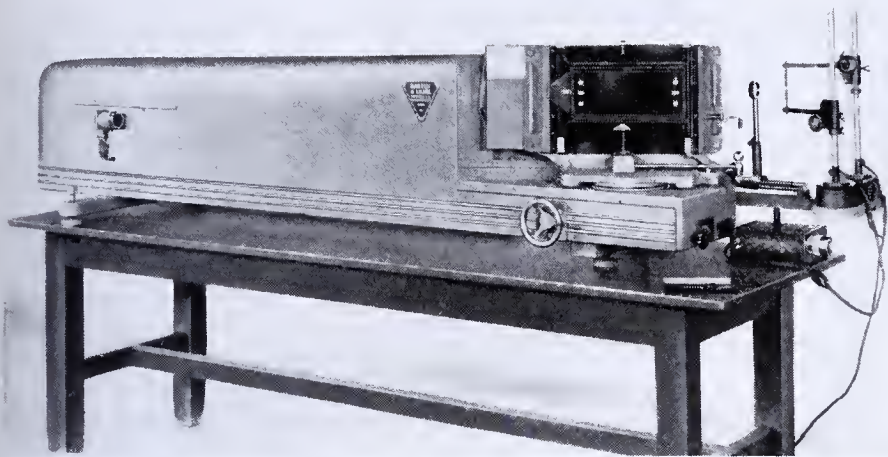
tration of known substances. They are valuable for the kind of information they may supply, for the speed with which required information may be obtained, and for the degree of accuracy obtainable in comparison with other methods. While comparisons are dangerous, one is tempted to say that the spectrograph is more useful to the chemist than all the above-mentioned instruments. It is deplorable that there is no word which includes both spectroscope and spectrograph. In spite of the fact that the spectrograph with its permanent photographic record of both visible and invisible portions of the spectrum is the most commonly used, the spectroscope is too useful to be ignored. The reader should interpret the word "spectrograph" in this article to include spectroscope and spectrometer unless it is obvious that only the photographic form is meant.

For years the spectrograph was the physicist's most powerful tool in his search to unravel the secrets of the construction of matter, and unaided it led him to the necessity for recognizing orderly arrangement in the complex structure of the atom. Lockyer in 1873 for the first time advanced the theory that changes in line spectra, due to rise in temperature of the source, could be explained by the breaking up of the atom just as the transition from band spectra to line spectra may be explained by the dissociation of the molecule. The chemist soon recognized its power to reveal the composition of unknown materials and the astrophysicist made it his basic instrument. It has revealed the fact that the universe is apparently made up of the same chemical elements that compose the earth. Without the spectrograph it is impossible to imagine how we could have acquired any information whatever about the composition of heavenly bodies except what might have been gleaned from the occasional meteors which reach the earth. Matter, emitting or absorbing radiation which the spectrograph can analyze into its component wave lengths, reveals not only its identity but much about the state in which it exists. Distance is immaterial, provided enough light reaches the observer to affect the eye or the



STEINHEIL SPECTROGRAPH OF 1894





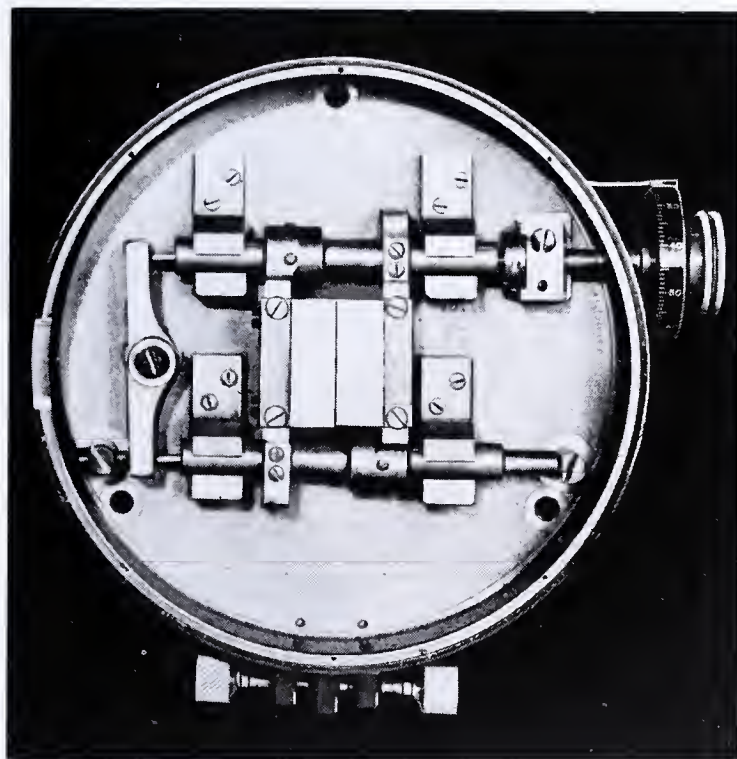
MODERN QUARTZ SPECTROGRAPH, LITTROW TYPE

utmost efficiency in operation. They must be adjusted in the factory and must maintain that adjustment during transportation and over a long period of possibly daily use. The operator must learn the mechanical technique of operation through the reading of some rather simple directions for use. In his hands the instrument must be dependable in spite of a certain amount of abuse, the worst of which is probably experienced when it falls into the hands of one who cannot keep his fingers off the adjustments. Finally, it must be powerful enough for the work required without excess power which leads to excessive cost and difficulty of operation.

photographic plate. The arc on the laboratory table or the distant nebula tells the same story.

So long as the instrument was useful only for qualitative chemical analysis, it was not of great value in the laboratory. Its major function as a qualitative instrument was in the identification of trace elements, the concentration of which was so weak that they defied ordinary chemical analysis. This period of spectrographic science dates from the time of Bunsen and Kirchhoff to about 1875 when Lockyer proposed its use for quantitative work. He was followed by Hartley in 1884 and Pollok, Leonard, and de Gramont about the turn of the century. These men laid the basis for quantitative analysis and since their time the science has been progressing so swiftly that one hesitates even to suggest what may represent the ultimate limits of its usefulness.

In the early days of spectroscopy, the investigator usually had to make his own instrument. In the graduate school of a university, where time is usually more abundant than money, this condition could be tolerated even though it yielded an instrument operable satisfactorily only by the one who designed and built it. For the modern industrial laboratory, where time is the most valuable element and the results of the new investigation or of the routine analysis are the all-important objectives, the design of instruments must offer the

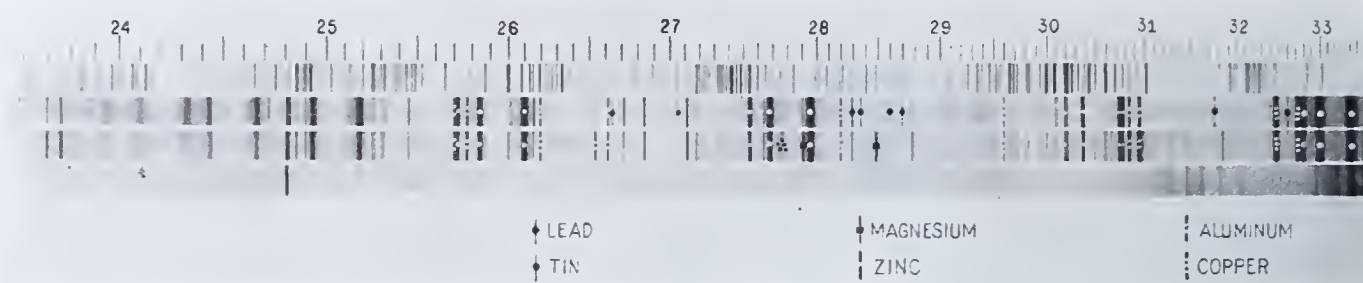


SLIT MECHANISM FOR LARGE SPECTROGRAPH

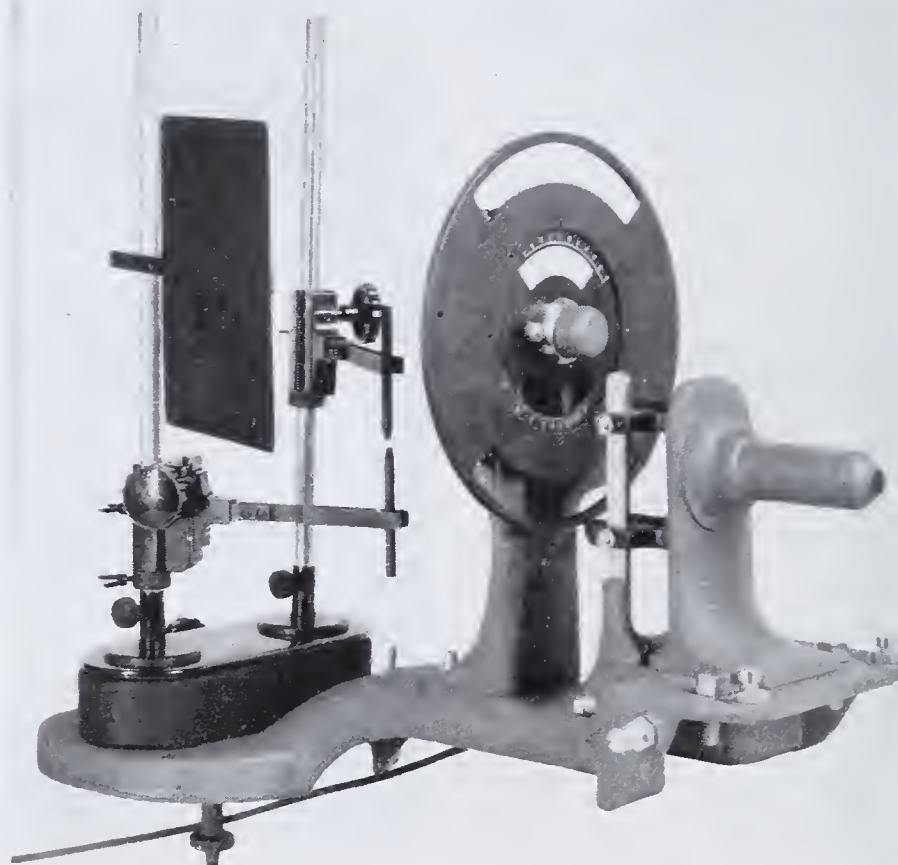


WAVE-LENGTH SPECTROMETER FOR VISUAL REGION





TYPICAL SECTION OF SPECTRUM AS TAKEN WITH QUARTZ INSTRUMENT



MODERN SECTOR PHOTOMETER FOR ULTRAVIOLET REGION

The present-day spectrograph is the joint product of the research laboratory, the instrument designer, both optical and mechanical, and the skilled mechanic. The fundamentals of the spectrograph came from the physics laboratory; the technique of application to the field of chemistry, from the chemical laboratory. From the fundamentals developed in laboratories of both groups, the optical instrument manufacturer has built an instrument which has perhaps made its most startling contribution in the field of metallurgy. The composition of a complex alloy may be completely determined in a few minutes from the time that the sample is taken and correcting alterations made while the furnace is on. Essential constituents may be determined quickly and with an increasingly high accuracy.

The task of the designer in this advance is to produce precision scientific instruments which have the speed, strength, and rigidity necessary to ensure unfailing performance under peak conditions of operation. For all practical purposes these instruments must exhibit the same reliability that is required of the modern automobile. New alloys and materials must be utilized to give lightness and at the same time preserve

the necessary strength. Noncorroding metals are substituted for the wood and iron which were common in early design. Increase in the speed of operation has been accomplished by providing designs in which motions are interlocked so that the operator accomplishes by a turn of the hand what formerly required several separate adjustments to do. Photoelectric apparatus has been designed for the quick evaluation of the photographic image, thus relieving the strain on the operator and affording him relief from visual fatigue.

The lines of investigation along which the designer must work, which are briefly indicated above, represent only one phase of his task—that of the primary instrumentation. There are in addition several auxiliary fields which demand his careful attention. Since in modern practice the results are registered photographically by the burning of a sample in an arc or a high-tension spark, they must depend for their accuracy and reproducibility upon the production of a constant set of conditions in such sources. He must, therefore, invade the field of electricity and design equipment of such a nature that the source variable can be neglected. This means that he must study arc and spark phenomena under various con-



ditions and determine the optimum for a particular problem. He must study the relations of inductance and capacity, and eventually he must be thoroughly acquainted with the influence of one element upon another when both are volatilizing at the same instant. Practically in the present status of spectrographic science this has become a limiting factor and is a problem, which, when satisfactorily solved, offers promise for greater accuracies than can now be attained. Physicists and chemists in various fields are seeking the answer and it is hoped that major advantages will come from these investigations. The Bausch & Lomb Optical Company is making the necessary plans to support a fellowship at the Massachusetts Institute of Technology, the sole purpose of which will be to investigate the basic phenomena occurring in sources of energy where metallic vapors exist. Such investigations as these provide the basis upon which the designer can rely to build into his mechanical, optical, and electrical structures new features which will increase the reproducibility and hence the reliability of the results. As is true with any growing science, many problems of fundamental nature are still unsolved and the solution of any one usually makes it necessary to redesign existing apparatus or to devise new apparatus to meet the need.

Another phase of design which is not often given enough consideration is that of the study of the materials in the optical structure. Today most of the work is done in the ultraviolet or in the infrared region where suitable materials are few and expensive. The designer must utilize these materials to the utmost and must be sure at all times that they

are neither inferior in quality nor poorly fabricated. This means that he must be, to a certain extent, a student of crystallography in order to design and test systems which will function to the greatest advantage and convenience of the user. Quartz, calcite, fluorite, and rock-salt all enter the optical structure in one place or another and each offers its own problem in the design of specific optical systems. Quartz and calcite are birefringent and the former is rotatory also. Each requires special forms of computation to produce the desired results. Rock-salt is hygroscopic and offers its own peculiar problems. Only careful selection of material and careful handling of the varied optical constants can achieve useful results.

The combined efforts of many individuals are usually necessary to bring about material advances in any scientific work. In this brief account of developments in a single group of instruments, we see the designing engineer drawing his data from industrial and educational laboratories, combining these with his own knowledge of materials and design, and turning back instruments which contribute to increasing accuracy and additional achievements in many fields. The chemist, the physicist, the astronomer, the biologist, the geologist, the criminologist, and even the dealer in scrap metal in one way or another derive profit from the joint efforts of the laboratories and the instrument designer. Whether it be the composition of the universe millions of light years away, or the composition of the discarded bit of alloy in the junk yard, the spectrograph is capable of yielding the answer quickly and in a manner that is not usually subject to dispute.

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## The Laboratory Supply House

D. A. KORMAN

Eimer & Amend, New York, N. Y.

**L**ABORATORY supply houses are not merely dispensers of merchandise. Very few people realize how far their service extends and how vital is their contribution to industry, science, and economic welfare. It is logical for laboratory workers to approach these institutions with their problems, for where else can such complete service be rendered? A staff consisting of chemists, physicists, bacteriologists, instrument makers, and glass blowers, with instrument shops, glass-blowing shops, literature references, files, and similar facilities, is maintained at great expense by these firms. The older laboratory supply houses are libraries of information, whose functions are to render willingly a practical service to those in the field who have perplexing problems.

We read of the progress made in developments of plastics, synthetic textiles, medications, etc., better materials produced at lower prices, better methods of preserving foods, purer foods, sanitary control, eradication of disease, increase in the span of life, creation of new industries, better homes, etc., all as a result of achievements by research. The significance of the contribution that is made by the laboratory supply firm is often overlooked entirely.

It is true that in the brain of the researcher ideas are created, but mental visions do not always become practical processes unless tools are developed or created to carry out the ideas. For instance, a scientist evolves a plan for manufacturing a new product. He finds during the development

stage in the laboratory that he needs a special piece of apparatus. Since he is no artisan and has no facilities for fabrication, he approaches a laboratory supply house, as a source that not only makes these available but is able to conceive what he has in mind. Thus, frequently the task becomes the problem of the artisan assigned to construct an apparatus that will finally carry the problem to success.

Some years ago, this company was approached by a scientist who had an idea that the product his firm was manufacturing could be improved in quality and produced more efficiently. He outlined his theory and explained the existing methods and processes, and in a short time a thorough knowledge and understanding of the problem were acquired by the artisans delegated to the task. It was necessary to devise an instrument for actual tests and control of the materials, and after many months of investigation and experimenting, the problem was solved most satisfactorily. The firm, thereafter, was able to produce a better and more uniform product, and the undertaking resulted in many economies and a tremendous increase in sales.

Though the role that was played by the laboratory firm has undoubtedly long been forgotten, it certainly contributed substantially and in many ways to the benefit of the industry. This is but one of numerous incidents where the research worker and industry have benefited by the scientist's co-operation.



# Analytical and Microbalances

A. W. AINSWORTH

Wm. Ainsworth & Sons, Inc., Denver, Colo.

VERY few users of analytical balances realize or appreciate what has been done in recent years to improve reliability and reproducibility particularly at the higher sensitivities, and it is the intention of this article to state some of the difficulties encountered in the efforts to give the chemist a more reliable piece of apparatus than has heretofore been obtainable.

The beam, being the most important part of a balance, has of necessity been given the greatest amount of attention, and during the investigation of the behavior of balance beams under varying conditions such as load, temperature, and humidity, some very interesting information has been obtained. The first important discovery was the great variation in the material (aluminum alloy) commonly used for balance beams, and after definitely determining these peculiarities, the finish was found to have a wide bearing on the

performance and stability of the beam. Various alloys, while varying from one another only in very small amounts, were discovered to behave in entirely different manners. Strains due to the mechanical working of the material itself were of major importance and it was during the above-mentioned investigations that a method of normalizing this material was discovered.

The actual production or machining of the beam from the blank material brought its attendant complications which were more easily surmounted but, nevertheless, contributed to some of the peculiar behavior of the beams. As these problems were gradually approached and carefully investigated, the question of the knife edges in relation to their attachment to the beam came to the fore, and it was during this particular investigation that a great deal was learned not only of the proper fitting of the edges to the beam but of

FIGURE 1. PRODUCTION OF BEAMS FROM BLANK MATERIAL  
(upper right)

GRADUATING OF STANDARD ANALYTICAL BALANCE BEAM  
(lower right)

ENGRAVING OF NUMBERS OF BALANCE BEAM (left)

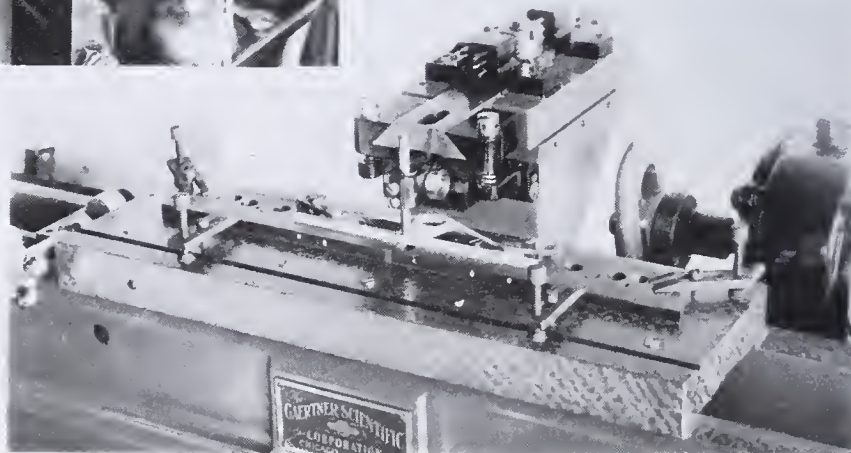
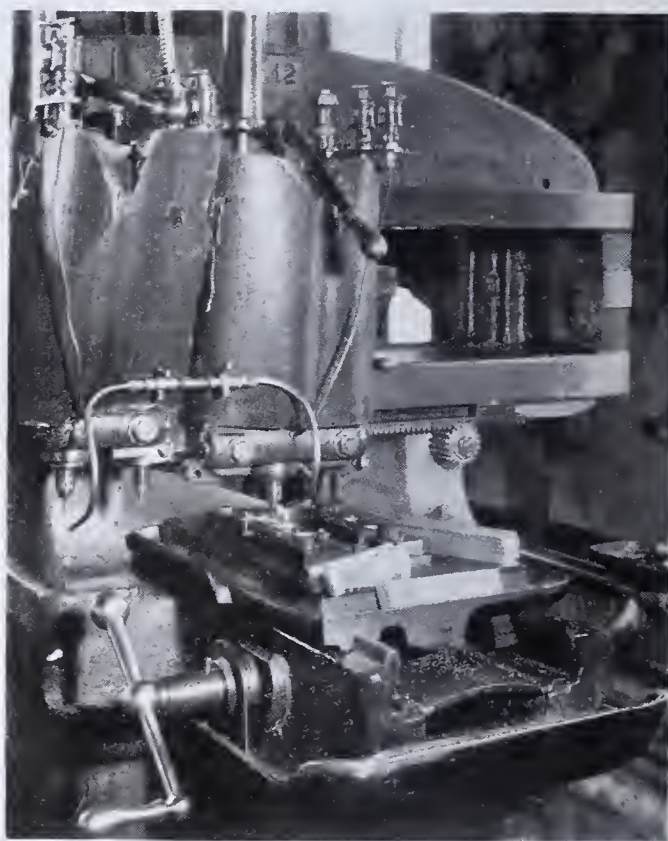
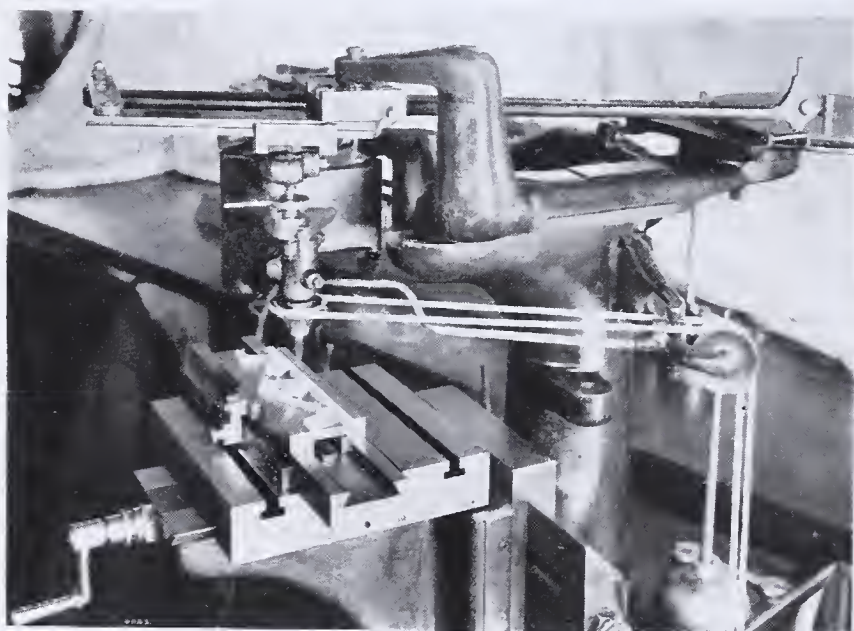
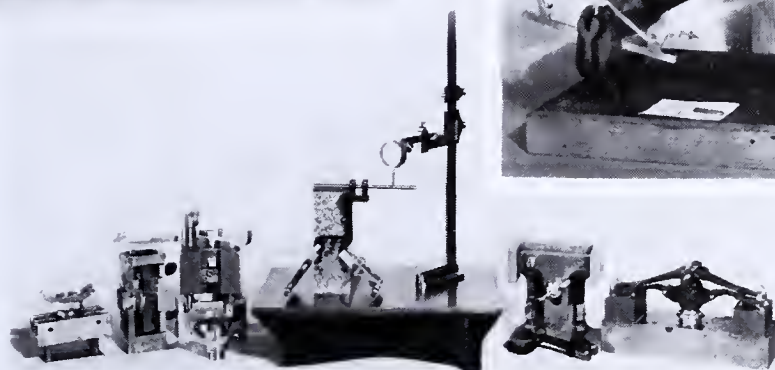
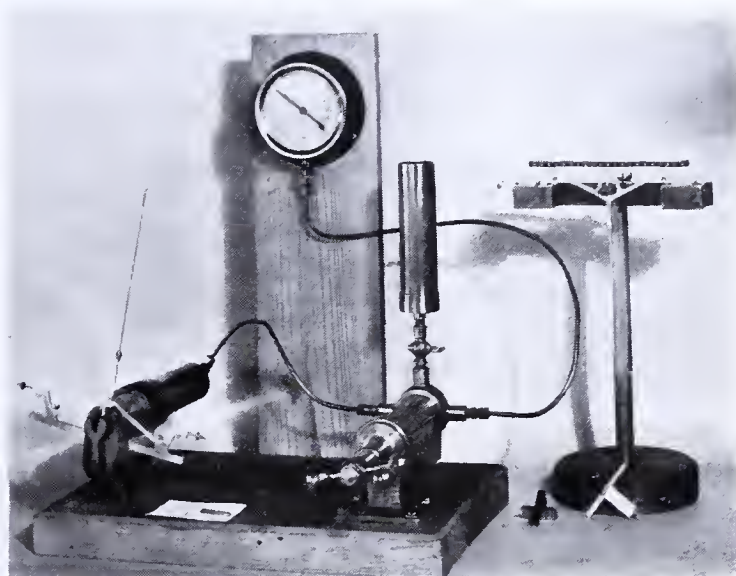






FIGURE 2. FIXTURES FOR GRINDING AND TESTING AGATE EDGES AND BEARINGS (left), SETUP FOR DETERMINING FIT BETWEEN AGATE EDGES AND BEAM (right), AND JIGS AND FIXTURES FOR CHECKING PARTS (bottom)



the proper production of these edges. The grinding of the infinite knife edge, which is the actual support medium of the load suspended by the beam, is important, as the behavior of the beam is due very largely to the accuracy of this edge. Various methods of grinding and polishing this contact edge have been tried, with the result that balances have been constructed of a higher sensitivity and capable of handling heavier loads than have previously been possible. The various devices used in determining the qualities and qualifications of the agate knife edges were rather ingenious and original. Other important problems that presented themselves were the accuracy of the graduations and the numbering of the beams. It was found that where the numbers were stamped, the time required to obtain a stable beam was many times longer than when the numbers were engraved by actually removing the material with a revolving cutter.

To take advantage of these new refinements in the production of balance beams, more care was necessary in the design, production, and assembly of the parts used in connection with the beam-releasing mechanism. Many conditions not conducive of smooth and accurate operation of this part of the balance detracted from the improvements obtained in the beam; therefore, manufacturing jigs and fixtures had to be made to much closer tolerances than had been previously used. Machining operations changed, and improved inspection methods such as had been used only by the manufacturers of high-grade tools were adopted. These improvements, together with the use of metal cases, have made it possible to maintain close adjustments and alignment of the various parts of the balance.

The photographs of Figure 1 show (upper right) the production of beams from the blank material. The method adopted assures that a minimum amount of machining strains will be in the beam; two separate cuts are made—a

rough cut and a finishing cut. The graduating of a standard analytical balance beam is shown at lower right, a highly accurate graduating machine being automatically compensated for temperature; and at left, the engraving of the numbers of the balance beam.

Figure 2 shows (upper left) some of the fixtures for grinding and testing the agate edges and bearings used on the balance beams; (right) setup used to determine the closeness of the fit between the agate knife edges and the beam; (lower) jigs and fixtures for checking the various parts of the releasing mechanism, drop levers, etc., as well as a setup for continually inspecting the accuracy of the work as it comes from these fixtures.

A great deal of work has been carried on in connection with the development and production of a successful microbalance and at this time a number of microbalances are in use whose performance is extremely gratifying. The information that is being accumulated in reference to their performance under varying degrees of temperature, humidity, and barometric pressure will result in making available to the chemist balances capable of carrying greater loads at higher sensitivity with greater availability and reproducibility than has heretofore been available.

In connection with the investigation of the performance of microbalances, a very interesting development has been carried on in an effort to read more accurately the deflection of a microbalance beam, an entirely new principle being used. While this has not proved entirely satisfactory as a reading device, it has, nevertheless, brought to light some very interesting facts, heretofore unknown, regarding the actions of a balance beam. It is believed that the knowledge that has just been gained will lead to a more thorough understanding regarding the sometimes erratic performance of microbalances and will have its effect on the future development of the standard analytical balance.



# Laboratory Apparatus, Its Evolution and Development

WM. B. WARREN, Fisher Scientific Co., Pittsburgh, Penna.

**L**ABORATORY appliances, starting with the early crude forms shown in the accompanying illustration, have been improved in keeping with the advance of the various sciences to which they are so necessary. In fact, advance has been mutual; new discoveries in the sciences have led to the development of new laboratory tools, and in many cases, the development of a new tool has paved the way for great scientific advances.

The early chemist needed to be a versatile soul, for he had not only to plan and carry out his laboratory work, but also to be his own instrument maker. Chemist, machinist, glass blower, jack-of-all-trades—who knows what might have been the result had such great minds as those of Bunsen, Liebig, Lavoisier, and Kekulé been free to concentrate on the significant matters which they were uniquely endowed to pursue?

With the growth of early scientific work abroad came the inevitable advent of specialization and the appearance of the early instrument maker and glass blower. These men worked closely with those in the centers of scientific investigation and often played important roles by developing new apparatus or improving the older forms.

Since so many of the original workers in this country had studied abroad under the older chemists, it was only natural, when they started to carry out their studies or to teach here, that they sought the equipment which they had used abroad. Laboratories were still rarities, and those who supplied their requirements were mostly importers.

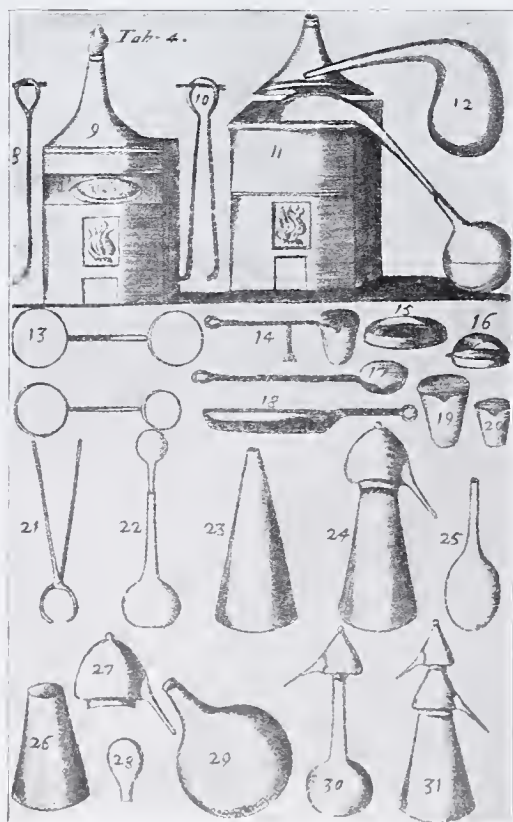
The advent of the Great War found us not only without a significant chemical industry, but also without an adequate

domestic source of laboratory apparatus with which to create such an industry. It was during the early war days that the American chemical industry, together with the American apparatus industry, began to develop to what it is today.

In the initial rush of war preparations, there was time to do nothing but manufacture prototypes of the foreign apparatus. No attempt could be made to introduce improvements: production was all-essential. Gradually production was stepped up until urgent needs were fulfilled and there was time available for development work. Good use was made of this opportunity, for with the close of the war not only had a new industry been founded, but it had rooted and grown to the extent that the laboratory worker found himself with a domestic supply of better glassware, more accurate balances, more highly refractory porcelain, and better reagents than ever before had been at his disposal.

This industry, today really only twenty-five years old, has grown and specialized just as have the industries and sciences which it serves. Certain organizations within the field have developed along specialized lines, while others have acted in the capacity of "service stations" where appliances made by the specialists are centered and distributed. A few combine development, manufacture, and service in one completely integrated unit.

It is natural that an industry in such close contact with science and scientists should profit from that contact, and the same thought methods, the same desire to uncover new facts, and the same critical attitude have prevailed in the laboratories of those making scientific apparatus.



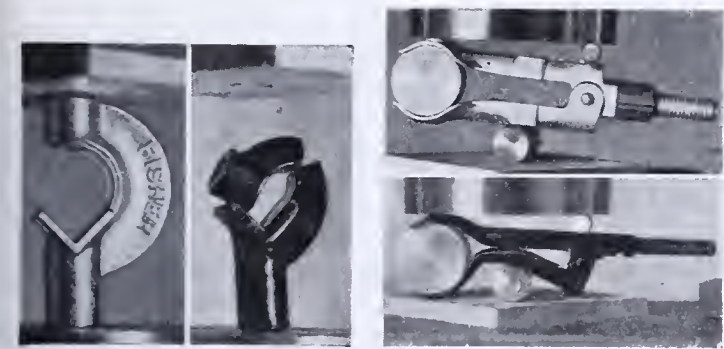
## An Explanation of the fourth Table.

- 8 **A** Hook to clear the Grate with.
- 9 A Testing Furnace.
- 10 A Pair of Tongs.
- 11 A small Reverberatory, or an open Furnace, for one Retort.
- 12 A Retort.
- 13 Iron Rings to cut Glasses withal.
- 14 A Cone, or Antimonial Horn.
- 15 A Test.
- 16 A Test with its Muffle.
- 17 A Ladle.
- 18 An Ingot.
- 19 A Crucible.
- 20 A left Crucible.
- 21 A Pair of Tongs to take a Pot out of the Fire withal.
- 22 Two Bolt Heads, or Matrasses, made a Circulating Glass of.
- 23 An uncut Body.
- 24 A Body and Head.
- 25 An Egg, or Oval Matrafs.
- 26 A Cut Body.
- 27 A Distilling Head.
- 28 A Blind Head.
- 29 A Ballon, or Receiver.
- 30 A Matrafs, with its Head.
- 31 A Body, with a double Head.

## EARLY CHEMICAL APPARATUS

[As depicted in "A Compleat Course in Chemistry", by Geo. Wilson, Chymist, printed in London in 1709, at the Judges Head in Chancery-lane]





DESTRUCTIVE TESTING TO EVALUATE DESIGN AND MATERIALS

In illustration of the activities of the writer's laboratory, a typical case of development of laboratory apparatus will be described.

Improvement of Laboratory Clamp

It has been wisely said that it is quite as important to know what not to work on as it is to know what to work on. Effort is obviously best directed toward apparatus of broadest application, and a study of the humble but ubiquitous laboratory clamp in all its forms was conducted in order that improvements might be brought about. The common faults of the typical clamp, which had been fabricated in the same way for so many years and yet had exasperated so many users, were brought to light. A survey of users was instituted and the chief faults reported were that they corroded, that the joints froze, that the pressed sheet jaws bent under load, that the screws and wing nuts lacked adequate strength, and that the range of size capacity was too limited.



RESULTS OF CORROSION TEST. CONTROL ON LEFT

The problem was then resolved into three phases: a metallurgical problem to be studied with particular attention to corrosion resistance in laboratory atmospheres, a mechanical problem to be approached after a study of the stresses involved in the use of clamps, and a design problem to be worked out after a study of the versatility, positioning, and gripping modes required by the various parts to be clamped. The metallurgical problem involved corrosion studies of all likely materials, using the ordinary laboratory clamp as control. Platings and finishes were studied in the same way. While no material or combination of materials could be found which was invulnerable to every possible laboratory environment, two were outstanding in comparison with the controls—brass and a strong zinc die-casting alloy. One element of the laboratory environment, mercury, is not usually encountered elsewhere and it was found that a double plating operation was very important to nullify its peculiar activities. The mechanical problem was attacked through destructive testing of models. Here much was learned which influenced the final designs.

The design problem was naturally conducted concurrently with the mechanical one and the designs most consistent with the requirements of strength, versatility, positioning, and gripping mode were finally evolved. Early in the course of the work it became evident that the forms would be complex and that they would have to be manufactured either from brass or bronze forgings or from

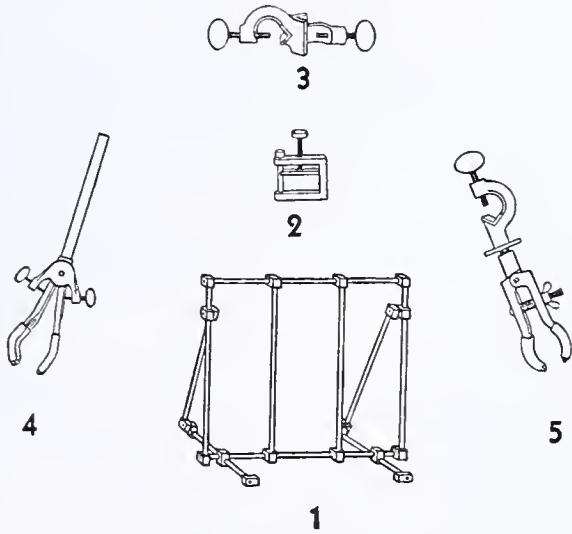
die castings. Forgings were economically unsuitable and die castings were chosen for those parts which were complex, while brass screw machine parts and tubing were specified wherever possible. Cooperation with the instrument shop and the die casters finally resulted in samples which were subsequently tested by the development laboratory. Before final approval, samples of all forms were submitted to representative users for trial under field conditions. Based on their suggestions further changes were made and, after final check with those who had presented suggestions, the models were approved and production was begun.

The responsibility of the development laboratory did not end here. Another of its functions is to continue to add new designs to the line, so that over a period of years new clamps and laboratory supports have been added as rapidly as laboratory tests and consultation with typical users have indicated that they will be useful and economical.

Functions of Development Laboratory

In the course of the development of some types of apparatus a great deal of experience with its uses is necessarily obtained. After an instrument is placed on the market the development laboratory has a further function in working with the potential purchaser in order that he may be able to determine how best to apply it to his needs. Such work has resulted in the development of new techniques and applications and in some cases in published papers.

Because of the breadth of scientific activity and the extent of its specialization, such a laboratory is an interesting and stimulating place. It is necessary to have staff members who are versatile in the extreme, yet who are well acquainted with the important details of many fields of scientific endeavor. This can be done only by careful selection of the personnel, and each individual must have at least one specialty and be able, withal, to work as did the early scientists, as a jack-of-all-trades.



LABORATORY APPARATUS SUPPORTS

- 1. Flexible frame support
- 2. Hose clamp for heavy-walled hose
- 3. Clamp holder
- 4. Adjustable clamp with three jaws
- 5. Clamp with rotatable jaws

The intense specialization which has developed in almost every line of human endeavor and especially in scientific fields, has resulted in special techniques and knowledge in every one of them. Often a method well known to one group of workers would be very useful if applied to the problems of another, yet is entirely unknown to them. The develop-



ment laboratory of the Fisher Scientific Company has taken upon itself the responsibility of serving, in so far as possible, as a sort of multiple liaison officer among the various scientific groups with which it has contact.

During the past decade there has been increasing application of the tools and techniques of radio and television engineering to the problems of the chemist. Recognizing this trend, and aware of the fact that the number of chemists who are adept in the construction of such apparatus is relatively small, the development laboratory has devoted a large part of its attention to apparatus of this nature in an attempt to make these valuable tools readily available. As a result there have already been developed a vacuum-tube voltmeter setup for a variety of titration applications, a photoelectric photometer for quantitative colorimetric analysis, and an instrument for analytical work by means of the dropping mercury electrode.

This line is being followed with diligence and work is now in progress pointing toward the application of electronic and electrical methods to other titration apparatus, to better temperature control of ovens and baths, and even to the determination of the carbon content of steel.

Biological chemistry has recently become very active and the development laboratory has paid a great deal of attention to this particular branch. Likewise, the needs of the hospital laboratory are being studied and present progress indicates that several new tools of value to workers in this field will shortly be available.

The whole line of laboratory apparatus on the shelves of the company is constantly being scrutinized with the intent of making improvements which may result in lower cost and greater utility.

While in the work on clamps cited above the development was initiated entirely within the organization, many others have their beginnings in suggestions of workers in the laboratory. Hence, close contact with the scientific world through reading its literature as well as through attendance at local and national scientific meetings is essential.

It is inspiring to believe that a real contribution to the advancement of science can be made by keeping the scientist supplied with the best possible tools. While it is only too true that "a poor carpenter blames his tools", it is equally true that a good workman produces finer work with finer tools.

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## Research in Instrumentation

PAUL SHERRICK AND LYNN D. WILSON

E. H. Sargent & Co., 155 East Superior St., Chicago, Ill.

THE research program in the laboratories of E. H. Sargent & Company is restricted as closely as possible to the field of instrumentation. This policy has a multiple objective, in that it maintains intraorganizational efficiency, directs the efforts of the company's personnel into the channels for whose exploitation they are best equipped, and avoids overlapping excursions into the theoretical province properly allocated to academic and the larger industrial research institutions. Obviously, the distinction between research in instrumentation and research in theory or analysis cannot be precisely drawn, and so the scope of activities is varied with each subject in hand in accordance with the degree of adequacy of pertinent theoretical or analytical knowledge initially available. This borderline flexibility is made evident below, in a typical case of extreme distortion into the analytical field.

A large proportion of the company's research work has a nature sufficiently repetitive and routine as commonly to avoid research classification. It occurs as essential activities in invention and design and its data accumulate as a group of facilities for production and service. Work of this classification is almost constantly carried on for investigation of (1) power transmission and conversion, (2) heat generation, transfer, and control, (3) electrical measuring and amplifying circuits, (4) service characteristics of materials and finishes, (5) measurement of physical constants, (6) accuracy limits and requirements of volumetric and gravimetric equipment, etc.

### Electrodeposition Studies

Distinct from this function which may be called routine research are the larger and more discrete programs of investigation required for the development or introduction of new analytical instruments of some importance. The company's

last completed program of this character was aimed at an acceleration of deposition rates in electroanalysis. The work on electrodeposition was initiated by a demand for electro-analytical installations expressly suited to high-speed routine analysis of nonferrous metals and alloys. The company was asked to solve a laboratory problem stated approximately as follows:

A group of laboratories analyzing a large number of brass samples a day, and having available in the literature as standardized procedures only the relatively slow-speed methods accepted as quantitative by organizations such as the American Society for Testing Materials, was faced with the economic necessity of reducing the principal time component entailed in the deposition proper. Necessity had forced these laboratories to explore the possible extension of deposition rates and to improvise such equipment and thereby to sacrifice a certain component of mechanical reliability and manipulative efficiency, since practically no instrumental equipment was available to accommodate high current densities. The study of instrumental requirements indicated a necessity for efficient circulation and cooling of the electrolyte, and an elimination of the mechanical hazard of overhead electrode rotating equipment. Furthermore, it was evident that the over-all efficiency of such a laboratory under its normal daily schedule was highly sensitive to the manipulative requirements of apparatus.

A protracted program of design yielded satisfactory solutions of all the principal mechanical difficulties and resulted in sufficient simplicity, flexibility, and durability for the heavy duty to be imposed upon it.

**SOLENOID STIRRING.** Solenoid stirring has been found distinctly advantageous for high-speed electrodeposition. Its investigation was occasioned by the two principal shortcomings of electrode rotating devices—namely, susceptibility to corrosion from rising acid vapors and delicacy of the alignment requirements when rotating the anode within the cathode. The solenoid method is far from new and was suggested by the publication of Heath (1).



This system was tested by the experimental construction of a great many different solenoids and an optimum result finally secured from a coreless solenoid constructed entirely of nonmagnetic materials and having the following approximate specifications: wire, No. 22 B. & S. gage, enameled copper; turns, 6500; resistance, 150 ohms; winding diameter, 7 inches; core space diameter, 3.375 inches; coil height, 3.5 inches; voltage, 110 direct current; current 0.75 to 1.0 ampere. In the center opening of this solenoid is inserted a close-fitting annular metal water jacket, which in turn surrounds a nonmagnetic stainless-steel beaker well. This cooling arrangement serves the dual function of preventing large temperature rise, resulting from efficiency losses in electrolysis, and at the same time of rapidly dissipating heat produced within the solenoid itself.

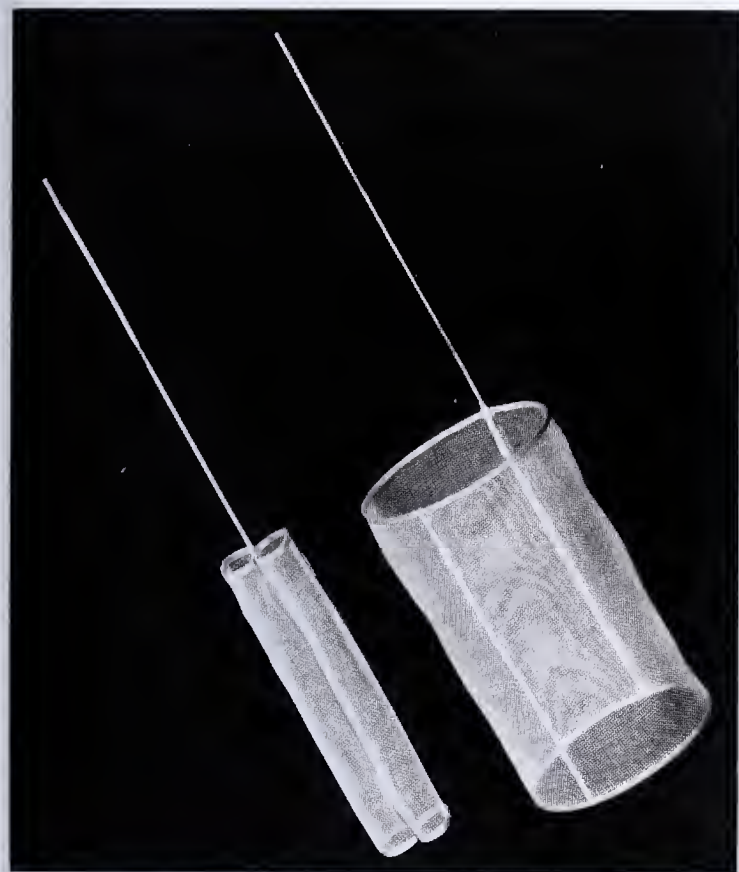


FIGURE 1. ANODE AND CATHODE FOR SOLENOID STIRRING

It is noteworthy that in addition to its structural and manipulative advantages, solenoid stirring is self-adjusting in the sense that increased current densities automatically produce increased rotation rates.

**ELECTRODES FOR SOLENOID STIRRING.** To employ high current densities large electrode area is essential, since the practical limit for production of good metal coatings is in the vicinity of 0.5 ampere per square inch of effective electrode area, assuming 52-mesh platinum gauze. The same requirement obviously requires a gauze anode. Having determined the maximum practical cathode area, attention was focused on the anode with the aim of bringing its area to a value as nearly as possible equivalent to that of the cathode, and, at the same time of producing a form which would best facilitate thorough mixing under the influence of the motor torque produced by the interaction of magnetic field and electrodepositing current. It was noted that the conventional cylindrical cathode allowed a relatively stagnant condition of the electrolyte confined within it and that diffusion from this quiet area into the rotating stream between cathode and anode was undesirably slow. A special anode form was therefore arrived at by experimentation, consisting of two elliptical tubes united as illustrated in Figure 1.

**SIMPLIFICATIONS BY SOLENOID STIRRING.** Figure 2 illustrates the possibilities for instrumental simplification as a result of solenoid stirring. Superstructure is eliminated, the solenoids are easily confined beneath a stainless-steel work plate, electrodes may be rapidly manipulated in noncorrosive Bakelite heads operating on grooved rods with centering and depth stops, and control panels are easily condensed to otherwise wasted but readily accessible spaces.

**METHODS OF RESEARCH.** It was at once evident that while the means of applying high current densities to fast routine electroanalysis had been provided, little was known regarding the practical limits to which such increases of current density could be carried. Furthermore, the ultimate adequacy of the circulatory and cooling provisions could not have been ensured, except as applied under the high current density conditions which were initially assumed to be analytically feasible. It was unavoidable, therefore, to undertake to establish and validate rapid methods for the principal analyses wherever feasible and to establish the maximum current density limits that could be employed. This work was undertaken with full knowledge that it properly belonged in the sphere of the institutional analytical departments, but under pressure of necessity and in the known absence of essential data pertinent to the problem.

The results of this analytical research program comprise 25 electroanalytical procedures shown to be quantitative within the normal requirements for industrial nonferrous control work and offering substantial time-saving in most cases over previous authoritative procedures. It has been found possible, for example, in the deposition of copper from brass to employ a current of 8 amperes throughout most of the deposition, beginning and ending with 5 amperes. The deposit remains coherent and free from burns. In the determination of zinc in brass a current of 6 amperes is allowable and for the same metal in silicon bronzes a current as high as 9 amperes may be used without damage to the deposit. Similar marked increases in current densities with corresponding reductions in deposition time have been effected for many other metal determinations.



FIGURE 2. INSTRUMENTAL SIMPLIFICATION RESULTING FROM SOLENOID STIRRING



The following list of currents as specified in the company's high-speed procedures at present will indicate the saving of time that has been effected in other typical cases.

	Ampere
Copper assay	5 finished at 3
Copper and lead in silicon bronze	5
Copper in nickel-iron alloys	8.5
Nickel in nickel-iron alloys	7
Iron in nickel-iron alloys	4
Zinc	9
Iron in beryllium-copper	4
Nickel in beryllium-copper	7
Copper and lead in steel	5
Aluminum in zinc-base alloys	2
Cadmium in zinc-base alloys	2
Antimony	3
Nickel-cobalt	3
Mercury	3
Silver	3

These procedures have been prepared in mimeographed form for circulation to any laboratories interested in this subject. Formal publication of this work is not contemplated, inasmuch as time and facilities will not permit the collection of a sufficiently great volume of data to determine the ultimate limit of accuracy in these procedures.

### Polarographic Research

Current research in the company's laboratories is principally devoted to the establishment of analytical procedures by the polarographic method of J. Heyrovsky. In 1933, when European publications in the field of polarography already totaled well over 200, Professor Heyrovsky proposed that this company undertake to introduce polarographic instrumentation to American laboratories. The study of the subject, begun at that time, revealed its possibilities at a rapidly increasing rate until by 1937 it seemed urgently advisable to make the instrumental facilities and service available at least to those few who were then already engaged in polarographic investigation in this country. As the result of an agreement made with Professor Heyrovsky in that year, the company has established sales and service facilities for this equipment and has presented to all American laboratories the essential data required for its consideration.

It was evident from the beginning that in spite of the extensive literature applying to theoretical and special analytical phases of polarography, a large technical responsibility would be incurred by the company's laboratories, owing to the lack of detailed analytical procedures for the almost unlimited number of analyses for which such procedures can be devised. It was essential in advance of a general sales program to qualify personnel for consultation and methods of research in this field. The situation has been greatly relieved by recent publications in American journals, notably from such investigators as J. Heyrovsky, I. M. Kolthoff, V. W. Meloche, J. J. Lingane, Otto H. Müller, R. H. Müller, J. F. Petras, L. A. Matheson, N. Nichols, G. T. Borchardt, H. Adkins, F. W. Cox, R. M. Burns, O. Kanner, B. Gosman, R. L. Gorman, M. E. Droz, E. S. Peracchio, H. G. Petering, F. Daniels, E. R. Smith, and C. J. Rodden. References to publications of all these American papers, among others, are compiled in the complete bibliography of polarographic publications maintained by and circulated from the company's laboratories.

At present writing the greatest weight of this current publication is still directed at theoretical considerations and it is therefore necessary in most cases to base recommendations for the use of polarographs on methods of research currently carried out by the company's facilities.

The common question that is asked by prospective polarograph users is simply, "Can we advantageously determine constituents *A*, *B*, and *C* in a substance *D*?" and in most cases the direct answer to this question can be made most simply by submitting a completed detailed procedure for the desired analysis; because any a priori scheme for such an analysis that might be proposed on the basis of the apparent chemical problems involved requires experimental confirmation of quantitative validity.

This is especially true in polarographic procedures owing to incompleteness of data regarding reduction and oxidation potentials at the mercury electrode under a variety of conditions, to the impossibility of predicting accurately the anodic potentials that will exist under the proposed electrolytic circumstances, to solubility and stability problems in composite

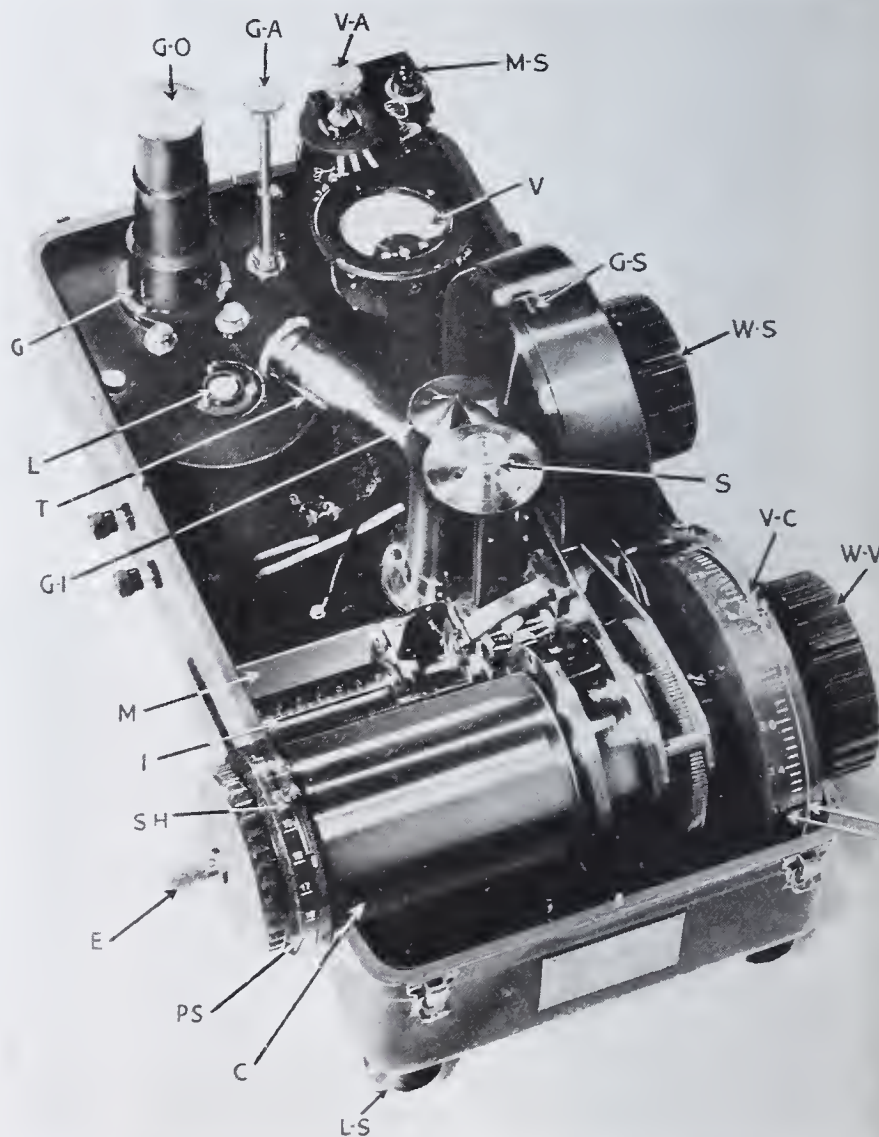


FIGURE 3. INSTRUMENTATION FOR POLAROGRAPHIC ANALYSES

- |                               |                           |
|-------------------------------|---------------------------|
| C. Photographic cylinder      | PS. Displacement scale    |
| E. Tightening bolt            | R. Slide wire bridge      |
| G. Galvanometer               | S. Speed adjustment       |
| GA. Galvanometer arrest       | SH. Shutter control       |
| GI. Galvanometer light source | T. Galvanometer telescope |
| GO. Zero adjustment           | V. Voltmeter              |
| GS. Galvanometer shunt        | VA. Voltage adjustor      |
| I. Exposure slit              | VC. Sliding contact       |
| L. Level                      | VS. Voltage calibration   |
| LS. Leveling screws           | WS. Shunt knob            |
| M. Mirror                     | WV. Winding knob          |
| MS. Master switch             |                           |



electrolytic solutions not always predictable, to the dependence of the discreteness of closely adjacent current steps upon the existing concentrations of the ions producing them, and, in general, to the novel viewpoint from which polarography requires the analytical chemist to inspect his problem.

**DEVisING POLAROGRAPHIC ANALYSES.** The peculiarities of the polarographic method are these:

Quantitative measurement is made by the production of a step in a current-voltage curve described under conditions such that the step height is determined by the diffusion rate of the ion being reduced and therefore by the existing concentration of that ion. The dropping mercury cathode employed in a solution containing an excess of other ions less easily reducible than the one momentarily measured provides the above-named condition and further assures a completely polarized cathode, due to which the voltage at which the reduction of a specific ion occurs is related to a thermodynamic property of that ion and is reproducible.

Measurement of the height of a reduction step provides the calculation of an existing concentration of the corresponding substance by comparison of this measurement against that of a step or a step increment produced by a known standard.

Concentration of the substance being determined is unchanged by the analysis.

The determinations of a number of constituents may be made in one polarogram subject to the following general conditions: (1) All substances are in solution in stable ionic states; (2) all substances produce reduction voltages at the mercury cathode within the working range of a 2- or 4-volt bridge; (3) the reduction voltages of all substances are spaced at sufficiently wide intervals; and (4) no substance is in a concentration substantially greater than that of any of the other substances following it in the reduction order. The essential instrumentation is indicated by Figure 3.

This apparently simple set of conditions is found to tax the ingenuity of the analytical chemist attempting to establish a procedure that will effect the greatest possible saving in time in comparison with the more conventional gravimetric or volumetric procedures. In each instance a number of routines are feasible, but almost invariably one of them will eventually be found to require a definite minimum of manipulation and time. Furthermore, the polarographer must always keep in mind the justifications for polarography. If a polarographic procedure is worth devising, it must be faster and less laborious than a corresponding conventional analysis leading to the same approximate accuracy or it must offer an analytical possibility not easily to be secured by the gravimetric, volumetric, or colorimetric procedures. In its microapplications the polarographic method is likely to be found, in many cases, roughly equivalent from the standpoint of time and accuracy to such spectrophotometric methods as may be established for similar work. In such an event the polarographic option may offer the advantages of a lower equipment cost and of a less exacting specialization in technique on the part of the operator.

The most active interest in securing what are sometimes called cookbook procedures in this field is naturally among industrial laboratories where the constant pressure of limited time exists and where new problems are continually challenging the existing knowledge of analysis. Accordingly, the company's present work is planned to produce a group of procedures for certain of the most common routines of industrial laboratories, such as those in metallurgical enterprises. A procedure for complete analysis of zinc-base die-casting alloys, determining copper, lead, cadmium, tin, iron, and aluminum is to be ready for early publication. Results to date indicate the probability of producing all the determinations in either two or three polarograms with a total of no

more than two chemical separations. The possible saving in time that such a method will yield is, of course, evident.

At present the program of research is being confined to problems of rather broad nature and wide interest. In view of the almost unlimited application of the polarograph to the solution of highly specialized problems and the increasing demand for such information, it is hoped that some of this work will be undertaken in the regular course of research at educational institutions.

### Literature Cited

- (1) Heath, G. L., *J. IND. ENG. CHEM.*, **3**, 74 (1911).

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## Research on Optical Instruments

C. W. BARTON, *Spencer Lens Company, Buffalo, N. Y.*

**E**ARLY in 1937 the Spencer Lens Company (Scientific Instrument Division of the American Optical Company) found it necessary to expand all facilities to meet a growing demand for optical instruments. A well-organized and competently manned Research and Development Division was the first step in the program and over eighty specialists and technicians have been employed since that time.

The division has three main functions—research, engineering, and model making—with a personnel to perform, adequately, the specific tasks under these functions. The model-making function is handled in two separate departments, one making the special optical parts and the other the mechanical parts.

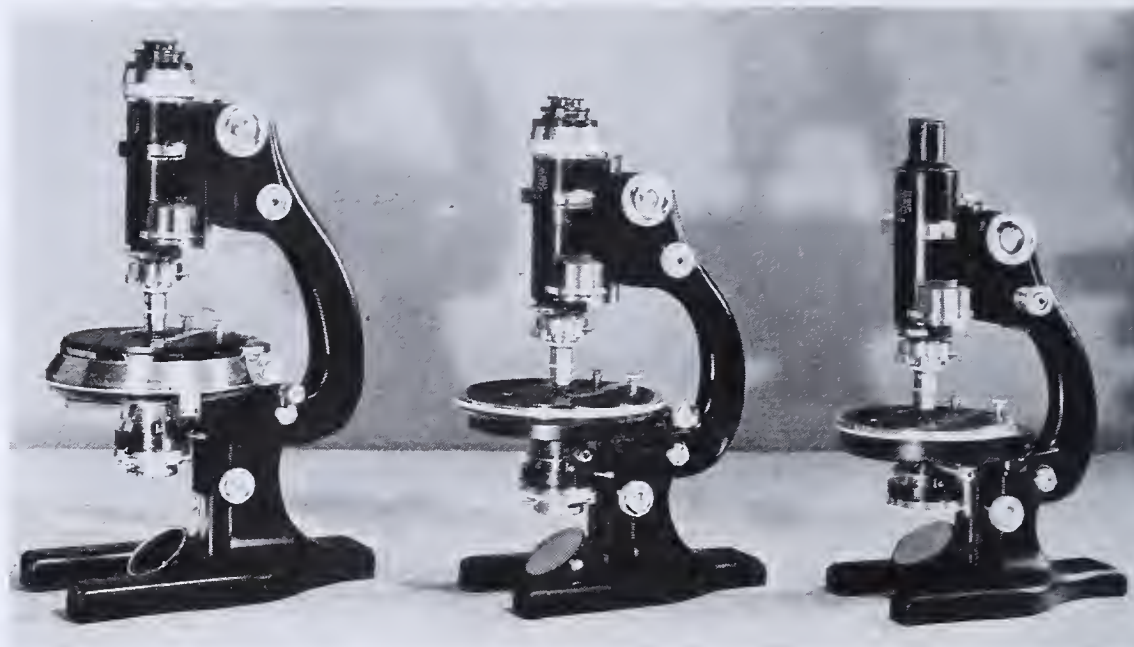
A research library, with a trained librarian in charge, ensures availability of reference data and rapid circulation of current scientific and technical literature.

The fundamental research work by members of the Research Department is reported periodically before the scientific and learned societies to which the men belong, and comprises both pure scientific endeavor and research directly related to Spencer products. Contributions to science include lens aberrations, resolution of objectives, growth of organisms, biomathematics, radiometry, color theory, crystal optics, and band spectra. Cooperative research with other laboratories has led to mutual advantage in certain problems.

In addition to the ideas arising from the company's own research work, projects for the Research and Development Division frequently originate in the industrial, educational, research, or governmental laboratories of the country. Scientists or laboratory workers occasionally need equipment which is not commercially available and request assistance from the Spencer Lens Company, either by direct contact or through a Spencer representative in the field. If the needed equipment is a suitable product for the company to manufacture, it may become the subject of a problem, and be assigned to a member of the research staff.

The man who receives this responsibility may consult the other members of the staff to obtain the benefit of their background and broad experience. A group may be formed of several men chosen from the various departments of the Research and Development Division.





POLARIZING MICROSCOPES

The usual order of work on a project is to survey the field and decide on general principles, necessary precision, and optical and mechanical features. Drawings are then prepared and a pilot model is constructed under the supervision of the Engineering Department and given a rigorous test under operating conditions. This severe, practical testing is to ensure stability, accuracy, convenience, durability, and suitability for the task for which it was designed.

The pilot model may be sent to other laboratories to be certain that it meets the demands for which it was designed. Only after it has been improved as much as possible is it approved by the Sales Division and turned over to the Production Division for manufacture.



DIRECT-RESULT COLORIMETER



SPENCER DELINEASCOPE

In pursuit of their work, the men in the Research Department have greatly simplified optical computation. A careful study of existing colorimeter designs has made possible the development of a simplified optical system for the colorimeter. Improved methods of measuring ventilation and the flow of heat have been devised, reducing temperatures and increasing illumination in projection instruments.

Methods have been developed for testing optical glasses so that their optical properties can be specified within tolerances that will ensure a satisfactory product.

Microtome knives have been studied—sharpening methods, bevels, cutting angles, hardness, and grain structure—in relationship to biological problems. Spectrophotometric data have been applied to the routine quantitative determination of biological materials by colorimetric methods.



# The Testing of Chemical Balances

ARCHIBALD CRAIG, Mars, Penna.

VERY little has been written on methods of testing a balance for accuracy. The writer has found only one thorough treatment of the subject (1), written from the manufacturer's point of view.

A perfect balance should have a rigid beam, as light as possible for its capacity, supporting three straight and sharp agate knife edges exactly equidistant from each other, in the same plane, and parallel both horizontally and vertically.

The edges are made by grinding and polishing in two planes, so that the internal angle is a good compromise between sensitivity and durability. Most balances are finished with an internal angle between  $90^\circ$  and  $120^\circ$ . German makers prefer the sharper angle. American practice varies, but the most important makers prefer a more obtuse angle for ordinary analytical balances, and  $90^\circ$  for assay and microbalances.

The edge should be in a single vertical plane, and preferably a straight line. During repairs some edges are finished on a slightly convex plate. If there is equal curvature on both sides, the edge will be in a vertical plane but low in the middle. This gives high sensitivity at first, but the edge rapidly becomes dull.

Makers prefer to get high sensitivity by cutting out some of the middle of the edge rather than departing from the straight line. A convex edge, resting on a short part of the middle, permits the beam or stirrup to twist when free, and is intolerable.

A perfectly sharp edge is an impossibility.

Even when new, an edge should be microscopically rounded, so that it rolls over the plate instead of turning on a line. As a result of the rolling movement of a dull edge, the bearing lines of all edges are shifted, the middle in one direction and the ends in the other, so that the effective beam length on the high side is longer. That increases the speed of the swing, but as the displacement reaches zero when the beam is horizontal, dullness is not in itself a cause of error.

When the rounding is large, the stirrup is thrown off center by the turning of the edge, causing it to tilt, but this movement is opposite to that of the beam, so that the temporary beam error is partly corrected.

A serious result of the rounding of a dull edge is that when weights are displaced to right or left on the pan the tilting of the stirrups may be unequal, and cause a notable shifting of the rest point. Theoretically this should not occur, for there is a joint in the hook of the stirrup which should keep the stirrup plate level even when the pan is aslant. Friction in the joint, however, is often enough to cause tilting and consequent errors in weighing. The only balance which is fully guarded against such tilting is the Austrian Ruprecht, which has knife-edge bearings in the pan supports below the stirrups. It is important with other balances to see that the hook swings freely.

Balances which have grooved stirrups suffer more displacement when dull than those which have flat plates, as the edge tends to climb up the curved face of the stirrup agate and rest on a line farther from the middle of the edge than is possible with a flat plate. Such balances should be avoided except for rough work.

As the edges wear down, the end bearings become lower than the middle, causing a lowering of sensitivity with increased load. When weighings are finished by measuring the deflection of the pointer, there should be no such variation, or else it should be charted for different weights.

The lowering may be expressed as the ratio between (a) a

definite amplitude of swing with empty pans (say, 5 divisions of the scale of an ordinary American balance, or 2.5 divisions displacement of the rest point), and (b) the amplitude with a definite weight added (say, 100 grams).

In ordinary rider balances used to weigh to 0.0001 gram, the ratio should be as much as 5 to 4. A balance used for rough work, particularly for weighing out, where only small weights are used and the counterpoise is adjusted to rapid swing and low sensitivity, is not affected either in speed or accuracy by dullness of the knife edges, if the edges are smooth and not irregularly chipped.

It is possible to set the end edges higher than the middle, so that weight on the pan causes the center of mass to rise and the sensitivity to be greater than when the pans are empty. This is tolerable, except for deflection reading, within a narrow range, say 5 to 5.5, but it is evidence of unskillful work.

If the edges are tilted front and back with respect to each other, the beam length is not directly altered, but there are other bad results. There is an increased lag in the swing. The stirrup tends to shift when freed, increasing the error due to horizontal parallax. The wear on the edges is increased with danger of chipping. The edges should be free from tilt within visible limits.

If the edges are out of parallel horizontally, so that one end of an end edge is farther from the middle edge than the other, the effective beam length will change with every shift in the bearing point of weight on the edge. Such a shift may be caused by slipping of the stirrup front or back, due to a tilted edge or play in the lifting assembly of the stirrup.

Friction in the joints of the stirrup with shifting of the weights on the pan, front and back, is the principal cause of error from this parallax. The Ruprecht balance is well protected against this error by transverse edge bearings below the stirrups, but most other balances are subject to it when old.

The angular variation of the end edges from the middle should be not more than one minute of arc, and preferably a quarter of that.

## Tests

The following tests will be useful to show whether the edges of an old balance need sharpening or regulating, and to learn the condition of a recently repaired balance or a new balance of cheaper grade. Some balances on the market are well designed and of good material, but carelessly built. Some of them are very good and are well worth buying if the bad ones can be discovered in time and rejected.

**EDGES.** If an edge is chipped, it can be seen with a  $10\times$  lens, and felt by drawing the edge of a fingernail along it. A few nicks will not affect the use of the balance, if there is still some of the original edge on both sides of its middle. If the bearing is on broken parts there will be an erratic swing and failure to repeat.

A sharp edge may be known by its ability to plane off a real shaving, not merely crumbs, from the thumb nail. A straight edge will make a clean sweep of a film of oil spread on an optical plane surface. A plane piece of glass can be bought from a manufacturing optician. Approximate results can be obtained by taking several small pieces of plate glass, at least 0.3 cm. (0.125 inch) thick and 1.25 cm. (0.5 inch) wide, cleaning them well, and pressing them together two at a time. The interference bands will show which are most nearly flat. If one is found which has straight lines in one direction, so that a straight edge will sweep it, it will do.



After an edge is shown to be straight, it can be used to test the middle bearing plate of the balance. This is particularly necessary in old balances which have two plates on the pillar. They may both be flat but not in the same plane, and if so they will soon spoil a sharp edge.

A straight edge will clean the plate when slanted in either direction, but one that is curved may give two different impressions. A gap in the middle of the edge is a good thing if it is not more than one third of the total length, and if the rest of the edge is in a straight line.

If a balance has edges dull but still able to make a clean sweep of the plate, it should be saved if possible for rough work, as such edges are practically indestructible.

**BEAM LENGTH ERROR AND LEVEL OF KNIFE EDGES.** Find the rest point with the pans empty. Add 1 mg. and record the deflection. Put 100 grams on each pan, add weight to the original rest point, reverse the weights, adjust again, and record half the algebraic sum of the two corrections. Now add 1 mg. and record the deflection.

The beam length error is measured by the correction made necessary by the added weight. In a good new balance it will be not more than 0.2 mg. per 100 grams. An error of more than 1 mg. should not be tolerated.

If the edges are level with each other, the deflection per milligram will be the same with or without the 100 grams. This will be the case with a good new balance. For an old balance used for fine work it should be not lower than 5 to 4. For a repaired balance it should be at least 5 to 4.5. Ends slightly high, as much as 5 to 5.5, may be tolerated for a rider balance. It will take them longer to get low.

**TILTING OF KNIFE EDGES AND VERTICAL PARALLAX.** Take a small piece of plate glass, about 0.25 cm. (0.1 inch) thick, 4.25 cm. (1.7 inches) wide, and 15 cm. (6 inches) long, test it with a micrometer to make sure that it is of equal thickness at the corners as evidence that its faces are parallel, and with parallel jaw pliers chip away a rectangular gap in one side of it, 1.25 cm. (0.5 inch) shorter than the distance between the middle and end knife edges. The gap should be deep enough to permit the projections to cover the full length of the two edges without touching the beam or its attachments.

Cut off one end of the strip to leave a projection that will slip through the beam and cover the middle edge with room to turn. Correct the length of the gap at the other end if necessary, so that the other side of the other end will rest freely on the end knife edge.

Get reflected light along the glass, hold the plate firmly on the middle edge, and tilt it until it touches the end. A jeweler's loupe may be used for better vision. If no tilting of the edge is visible, the parallelism is sufficiently good.

The test for tilting can also be made gravimetrically as described below.

**HORIZONTAL PARALLAX.** Take a smooth wire paper clip, straighten it, and bend it double about 2.5 cm. (1 inch) from one end, so that the two legs almost touch. With the doubled end make a right-angle hook about 5 mm. long. Hang this hook on the lower cross bar of the stirrup if the bar is horizontal. If it is not, fasten a narrow strip of metal across it to make a support for the hook.

Measure down to the regular hook on the stirrup, and make another hook turned up, leaving it just long enough to hold the pan. Hang the pan on this hook, put the stirrup in place, and then bend the hook around until the pan hangs free. Bend the free end of the wire so that it will pass both the regular stirrup hook and the pan bow with the least interference, and bring it straight down so that the whole will hang vertically. Cut another clip for a counterpoise.

Tilt the double hook slightly so that the weight of the pan will rest entirely on the wire from the lower hook. Measure the length of the knife edge and the inside length of the stirrup bar. Open the double hook to a width that will throw the weight of the pan slightly inside the stirrup frame, and under a point just inside the end of the knife edge. Measure the distance between the position of the supporting wire of the hook when at one side

of the stirrup and its position at the other side. In most balances this distance will be from 6 to 7 mm. The distance can be kept constant by setting the hook each time with the free wire against the side of the stirrup.

Set the hook at the back of one stirrup and hang the pan on it. Put the counterpoise wire on the other pan, disregarding a slight difference in weight. Make a weight correction to zero rest point, hang the pan in the front of the stirrup, and correct again. Record the difference in the weights.

Test the sensitivity—that is, the deflection per milligram—of the balance for both positions, if the glass plate test is not used. If the two edges are level with each other the sensitivity will be the same. It should not vary more than 5 to 4.5.

The difference in weight of the two pan positions should be not more than 0.5 mg., though two or three times that will not cause any serious error. It is not uncommon to find repaired balances with an error of 30 mg.

The angle of parallax can be calculated from measurements. For example, on a balance with a 40-gram pan and a 7-cm. beam arm, taking a distance of 7 mm. on the knife edge, 1-mg. variation in the weight of the pan indicates an angle of 51 seconds.

For inspection the weight difference will be sufficient.

Balances of the Sartorius type, which have stirrups pivoted to tilt front and back, need special treatment. Set a small metal plate on the plate holder of the stirrup to lift the pivots slightly and prevent tilting. Tie the parts together, keeping the thread away from the agate plate, take off the loop below, and substitute one made of wire of the same length down to the hook, with two notches 7 mm. apart. The pan can then be hung in two positions, and the parallax determined.

Schulze's method of testing for parallax is to take off the stirrup and hang the pan by a hook on the knife edge. Some balances have enough overhang of the agate to hang a loop of wire on the end of the edge with a hook below. If this cannot be done, a grooved hook can be made to fit over the end of the edge, with another hook below to support the pan under the end.

The writer prefers in all cases to have the stirrup in position, both to protect the edge, and to make sure that the supporting points are in the true edge, and not in an accidental irregularity.

**LIFTING MECHANISM.** When the beam is lifted, each knife edge should be separated about 0.0125 cm. (0.005 inch) from its plate, with weight on the pans. A slip gage can be used, or a sheet of ordinary note paper. The paper should slide in freely, as most papers are slightly less than the given thickness. After inspecting the middle gap a fair guess may be made at the gaps under the stirrups, which may be hard to reach.

The lift should be vertical. A gap should not show at one end of the knife edge before the other, and neither the pointer nor the stirrups should show any tilting when raised. This is highly important, for a tilt greatly increases the danger of chipping and battering the edge. Too large a gap is bad for the same reason. The given gap measurement is a maximum, to make sure that there will always be some gap. If there is no gap, the edge will wear against the plate from the vibration of the building.

The stirrups should be perfectly centered above the knife edges, so that they will have no sidewise tilt when let down.

A sidewise kick of the pointer when lifted is evidence that the stirrup lifts are either unequal in height or not vertical.

**PAN RESTS.** Pan rests which work by gravity need little attention except to see that they move freely and hold the pans in the proper position.

Pan rests which are brought by levers into fixed positions should not be set too high, as they will cause the stirrup to tilt and may damage the edges.

## Acknowledgment

Acknowledgment is due to A. T. Pienkowsky of the National Bureau of Standards for advice and assistance in preparing these tests.

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# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Identification of Aluminum Hydrate Films Of Importance in Silicosis Prevention

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SILICOSIS develops rather quickly in rabbits exposed to air containing moderate concentrations of quartz particles finer than about  $5 \times 10^{-4}$  cm., but is completely prevented if aluminum powder is also present in the air to the extent of about 1 per cent by weight of the quartz powder. This protective action of aluminum powder was discovered at the McIntyre Porcupine Mines, and has been studied experimentally by Denny, Robson, and Irwin (1).

It has been established (1) that aluminum forms, in the lungs, a protective film upon the surface of silica particles which prevents them from dissolving, and thus prevents toxic effects. The seriousness of silicosis in the mining and foundry industries indicates the importance of identification of this film.

The smallness of the silica particles and the very small amount of aluminum (less than 1 per cent) which is sufficient to cover them with a protective film make it evident that this film is extremely thin. An estimate of its thickness can be readily made from available data.

For a spherical particle of diameter  $D$  covered by a film of thickness  $t$ , assumed much smaller than  $D$ ,  $t/D = fM\Delta/6$ , where  $f$  ( $<0.01$ ) is the ratio of the mass of aluminum in the film of unknown composition to the mass of the silica particle,  $M$  is the ratio of the molecular weight of the film to the molecular weight of the aluminum in one molecule of the film, and  $\Delta$  is the ratio of the density of silica to the density of the film. In this expression  $\Delta$  is of the order of unity and  $M$  of the order of 3. Silicosis is produced by particles for which  $D$  lies in the range between 1 and  $5 \times 10^{-4}$  cm., and solubility is prevented by an amount of aluminum which would make  $f = 0.01$  if the aluminum were completely utilized in forming films on silica particles. Setting  $\Delta = 1$ ,  $M = 3$ ,  $D = 5 \times 10^{-4}$  cm., and  $f = 0.01$ , one obtains  $t = 25 \times 10^{-7}$  cm. = 250 Å. Because many particles are smaller than  $5 \times 10^{-4}$  cm., and available aluminum is surely not entirely used in forming film as is assumed by setting  $f = 0.01$ , it is certain that protection is afforded by films on silica particles many times thinner than this calculated upper limit of 250 Å.

This estimate gives 250 Å. as the thickness of a film which will certainly prevent solution of silica and toxic effects. The minimum thickness of film which will prevent solution is probably very many times less than this figure.

Considerations such as these, indicating that the protective film on silica particles can be extremely thin, led Francis C. Frary of the Aluminum Company of America to the view that electron diffraction analysis might be the best means of identifying the film. Such an investigation has been carried out by the authors in collaboration with Dr. Frary, and this paper presents an account of their part of the work.

They have found that the material which is precipitated upon silica by the reaction of water and aluminum is a hydrated oxide of aluminum. After drying, the film is crystalline and gives electron diffraction patterns characteristic of the variety of aluminum oxide monohydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) commonly called alpha-monohydrate in America, sometimes called boehmite, and identical with the natural monohydrate occurring in French bauxite. This conclusion from the authors' experiments has been stated in the second paper by Denny, Robson, and Irwin (1). The present paper contains a more detailed account of the electron diffraction experiments upon which the conclusion is based.

### Preparation of Silica Films

In electron diffraction studies one frequently obtains much clearer patterns when the primary beam of electrons goes directly through the specimen under examination than when the beam is scattered from its surface. On account of this superiority of the transmission method most of the electron diffraction experiments recorded here were made upon very thin films with the electron beam passing directly through them.

Films of silica, about 200 Å. thick, have been treated under various conditions with water containing aluminum powder. At the end of this treatment a film is caught, from the water surface upon which it is floating, across the jaws of a slit (for a photograph of this slit see 5, Figure 4) 0.05 mm. in width. This slit is mounted in the diffraction camera and, after the air has been exhausted, a beam of electrons is passed through the film and the resulting diffraction pattern recorded on a photographic plate. Features of this pattern are examined in order to identify the material formed upon the surface of the film.

The films of silica used in these experiments are prepared in the following manner. A glass microscope slide is first covered by gold vaporized in high vacuum from a V-shaped tungsten ribbon. Then immediately in the same apparatus silica is vaporized upon the gold from a second tungsten ribbon (3). Distances and quantities of gold and silica are adjusted so that the resulting composite film consists of a layer of silica  $2 \times 10^{-6}$  cm. thick lying upon a layer of gold  $30 \times 10^{-6}$  cm. thick. This composite film is large enough to supply a great many samples of silica which can be used in a large number of experiments. Each sample of silica is prepared, as and when required, by stripping from the glass slide a piece of the composite film 3 or 4 mm. on a side, dissolving the gold in a nitric-hydrochloric acid mixture, and then washing the remaining tiny silica film in several changes of distilled water.

Diffraction patterns from silica films prepared in this manner, not exposed to aluminum and water, are made up of diffuse rings characteristic of an amorphous material. There



are no sharp rings which could be attributed to unremoved gold. Measured diameters of the diffuse rings correspond by the Bragg formula to spacings of 3.6 Å., 1.95 Å., 1.2 Å., and 0.81 Å.

### Silica, Aluminum, and Water

**REACTION AT ROOM TEMPERATURE.** Many tests have been made upon silica films which have floated for various lengths of time upon surfaces of water maintained at room temperature in beakers which also contain small amounts of aluminum powder. This powder is a special grade of aluminum, supplied by Dr. Frary, which contains very little grease.

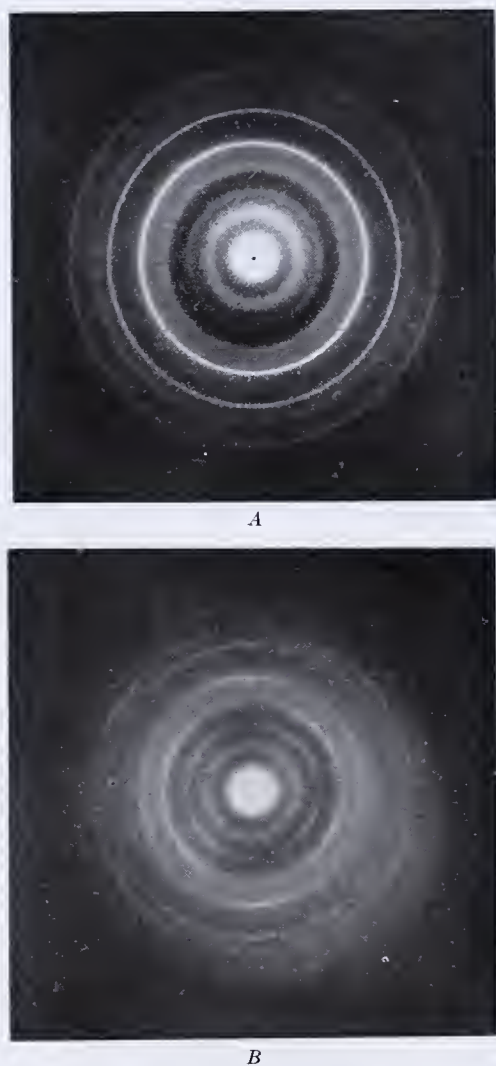


FIGURE 1. ELECTRON DIFFRACTION PATTERNS FROM SILICA FILM TREATED FOR 64 HOURS WITH ALUMINUM AND WATER AT 38° C.

- A. Electron beam normal to film surface  
B. Electron beam inclined 45° to film surface, by rotation of film about vertical axis

Because of its comparative freedom from grease it sinks in water, whereas ordinary aluminum powder floats as a mirror-like film on a water surface. The powder that floats on water cannot be used very conveniently with the authors' technique.

All silica films that have been treated with aluminum and water at room temperature have yielded diffraction patterns indistinguishable from the pattern from an untreated silica film. One concludes that there is no considerable, or at least no very rapid, production of a surface layer upon silica as a result of the reaction of aluminum and water at room temperature.

**REACTION AT 38° C.** Tests were next carried out at 38° C., approximately body temperature. Films of silica were

floated for various lengths of time upon water containing aluminum powder. Many of these films were greatly weakened or even broken up by this treatment, and in order to support them across the narrow slit it was in many cases necessary first to spread an auxiliary supporting foil across the jaws. For this purpose a foil of the plastic material known as Formvar about 200 Å. thick was placed across the slit, and the silica film to be studied removed from the water upon this foil.

Diffraction patterns from all silica films treated with aluminum and water at 38° C. exhibit rings which are more or less sharp. Diameters of these sharp rings are the same on patterns from all the silica films which have been treated with neutral or alkaline water containing aluminum.

Characteristics of these sets of rings, other than their diameters, vary with experimental conditions. The widths of the rings and their absolute intensities, as well as the widths and intensities of particular rings of a pattern relative to other rings of the same pattern, are functions of the duration of the chemical treatment, the pH of the aluminum-water mixture, and the material of the beaker in which it was contained. A description of these peculiarities and their interpretations will be given below, after the identification of the material giving rise to the patterns has been described.

In Figure 1, A and B, are reproduced diffraction patterns from a silica film which had floated for 64 hours upon water at 38° C. containing aluminum powder in a paraffin-lined glass beaker. The pattern of A was obtained with the film normal to the primary electron beam and that of B with the film inclined by 45°, rotated from the normal position about a vertical axis as the pattern appears here. The pattern of Figure 2 was obtained at normal incidence from a silica film which had floated for 44 hours upon the surface of a physiological salt solution, known as Locke's solution, containing aluminum powder and maintained at 38° C. in a paraffin-lined glass beaker. The appearance of Figures 1-A and 2 suggests that rings of the two patterns have the same diameters, and careful measurements confirm this indication.

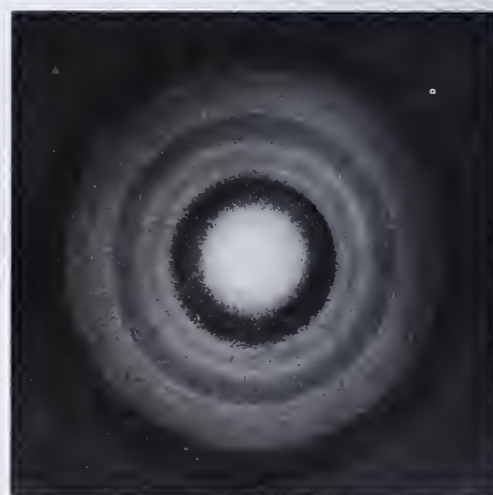


FIGURE 2. DIFFRACTION PATTERN  
From silica film treated for 44 hours with Locke's solution containing aluminum

In the first two columns of Table I are measured diameters and estimated intensities of the diffraction rings of Figure 1-A. In the third column are values of  $d$ , the corresponding crystal spacings calculated from the measured diameters,  $D$ , by means of the Bragg formula which, for these experiments, can be written in the form  $dD = 2L\lambda$ . Here  $L\lambda$ , the product of the specimen-plate distance and the electron wave length,



TABLE I. COMPARISON OF THE RINGS OF FIGURE 1-A, WITH X-RAY AND ELECTRON PATTERNS OF ALUMINUM ALPHA-MONOHYDRATE

Measured diameters Mm.	Electron Pattern of Figure 1-A Estimated intensities (arbitrary scale)	Crystal spacings Å.	Aluminum Alpha-Monohydrate				Crystal Planes
			X-Ray Pattern (from Table II)	Estimated intensities (arbitrary scale)	Electron Pattern (Table III, Figure 6)	Estimated intensities (arbitrary scale)	
			Crystal spacings Å.		Crystal spacings Å.		
10.3	9	Fuzzy band	6.2	10	6.3	4	.
12.8	1	3.66	..	.	..	.	.
14.7	7	3.18	..	.	..	.	.
20.1	6	2.33	3.17	8	3.21	7	.
..	..	..	2.35	8	2.34	6	.
25.3	10	1.85	2.06	3	2.04	1	.
26.3	1	1.78	1.98	2	..	.	.
28.5	1	1.64	1.86	8	1.88	7	3
..	..	..	1.77	2	1.79	2	.
32.6	9	1.44	1.66	3	1.67	3	.
..	..	..	1.53	2	1.55	1	.
35.7	5	1.31	1.45	4	1.45	5	5
..	..	..	1.44	3	..	.	.
38.5	2	1.219	1.39	2	1.40	.	.
..	..	..	1.31	4	1.32	5	.
41.3	8	1.135	1.260	1	..	.	.
..	..	..	1.210	1	..	.	.
45.8	1	1.023	1.180	1	1.172	2	.
..	..	..	1.161	1	1.155	3	.
51.0	3	0.920	1.136	2	1.042	2	8
54.6	1	0.858	1.119	1	..	.	.
56.7	2	0.827	1.050	1	..	.	.
..	..	..	1.028	1	..	.	.
60.7	2	0.772	0.954	1	..	.	.
65.6	1	0.715	0.935	1	..	.	.
71.0	1	0.660	0.925	2	0.909	3	12
..	..	..	..	.	0.856	2	.
..	..	..	..	.	0.832	3	.
..	..	..	..	.	0.803	1	.
..	..	..	..	.	0.774	1	.
..	..	..	..	.	..	.	20
..	..	..	..	.	0.666	1	.
..	..	..	..	.	0.614	1	.

by the supporting Formvar foil and the sharp rings by crystals of the hydrated aluminum oxide. A pattern from this same foil at 45° incidence contains, in addition to the diffuse rings, only short arcs crossing that diameter of the pattern which is parallel to the axis about which the foil was rotated; these arcs are portions of imaginary circles which have precisely the same diameters as the rings of Figure 3. Diameters of these rings are related to each other as the square roots of the whole numbers 3, 5, and 8, and they are furthermore the same as the diameters of the three strongest rings of Figure 1-A, which are designated by the numbers 3, 5, and 8 in the last column of Table I.

A considerably thicker layer of hydrated oxide was precipitated upon another Formvar foil with the aid of a potential of 3 volts between the slit, upon which the foil was mounted, and an electrode in the suspension. Diffraction patterns from this foil, at normal and at 45° incidence, appear in Figure 4. These are strikingly similar to the patterns of Figure 1, and measurements of the rings of Figure 4-A, disclose that there is excellent agreement between the two patterns with the exception of two rings of Figure 4-A, which are not present in the pattern of Figure 1-A. These are described below.

In still another experiment a foil of Formvar was treated in exactly the same way as the silica film from which the diffraction patterns of Figure 1 were



FIGURE 3. DIFFRACTION PATTERN AT NORMAL INCIDENCE  
From very thin layer of aluminum hydrate deposited upon supporting foil of Formvar

is known by independent calibration to have the value  $2.345 \times 10^{-6}$  sq. mm.

Identification of Protective Layer on Silica

The authors were induced by the work just described to carry out experiments upon hydrated oxides of aluminum. A solution of aluminum chloride in water was precipitated by ammonium hydroxide, and the resulting suspension washed by dialysis for 10 days; after this treatment a very small amount of hydrochloric acid was added. The suspension was found to be stable for a long period of time, and some of it was used in many different experiments.

In the first of these experiments a drop of the suspension was placed upon a Formvar foil lying across the 0.05-mm. slit, and the water was allowed to evaporate. The electron diffraction pattern obtained from this foil at normal incidence is reproduced as Figure 3. The diffuse rings of this pattern were produced

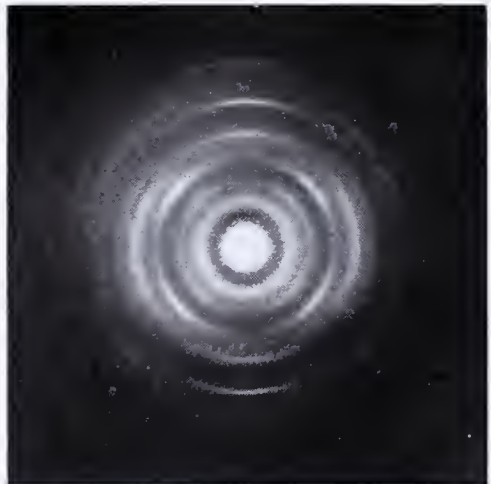
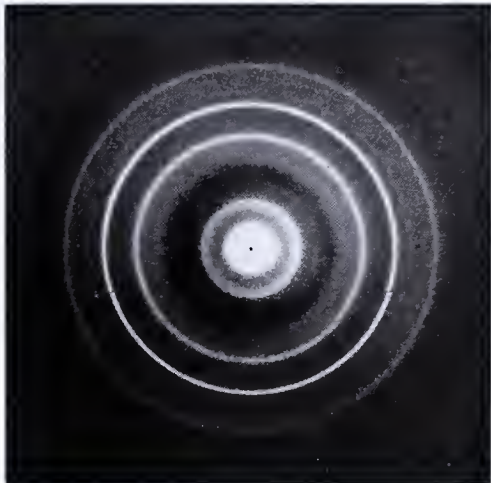


FIGURE 4. DIFFRACTION PATTERNS FROM RELATIVELY THICK LAYER OF ALUMINUM HYDRATE UPON FORMVAR SUPPORTING FOIL  
A. Normal incidence  
B. 45° incidence



TABLE II. DATA FROM X-RAY DIFFRACTION PATTERNS OF HYDRATED ALUMINA

Alpha-Monohydrate (Boehmite)				Alpha-Trihydrate (Hydrargillite)				Beta-Trihydrate (Bayerite)			
Measured diameters	Estimated intensities	$d$ , Calcd. as: CuK $\alpha$	as: CuK $\beta$	Measured diameters	Estimated intensities	$d$ , Calcd. as: CuK $\alpha$	as: CuK $\beta$	Measured diameters	Estimated intensities	$d$ , Calcd. as: CuK $\alpha$	as: CuK $\beta$
Mm.		Å.	Å.	Mm.		Å.	Å.	Mm.		Å.	Å.
28.5	10	6.20	..	32.9	4	..	4.82	33.3	5	..	4.77
50.7	4	..	3.14	36.5	9	4.85	..	37.0	10	4.79	..
56.2	8	3.17	..	40.8	6	4.35	..	40.6	8	4.37	..
68.6	3	..	2.34	53.9	2	3.30	..	49.7	2	..	3.21
76.5	8	2.35	..	57.0	2	3.13	..	55.3	6	3.22	..
87.7	3	2.06	1.85	67.0	2	2.67	..	65.8	1	2.72	..
91.4	2	1.98	..	73.8	5	2.43	..	72.4	6	..	2.22
98.0	8	1.86	..	75.8	5	2.37	..	75.3	4	2.38	..
103.1	2	1.77	..	79.7	3	2.26	..	80.7	10	2.23	..
110.2	3	1.66	..	83.3	3	2.17	..	90.3	3	2.01	..
114.9	1	..	1.43	89.2	4	2.03	..	94.7	4	..	1.72
120.6	2	1.53	..	91.5	4	1.97	..	105.8	7	1.73	..
128.1	4	1.45	..	94.8	3	1.91	..	111.0	1	1.65	..
129.7	3	1.44	..	102.0	4	1.79	..	114.3	3	1.61	..
134.8	2	1.39	..	104.8	4	1.74	..	117.8	3	1.57	..
144.0	4	1.31	..	109.4	4	1.68	..	127.3	4	1.46	..
150.9	1	1.260	..	117.5	1	1.57	..	134.2	3	1.38	..
158.0	1	1.210	..	128.2	3	1.45	..	140.6	4	1.34	..
163.1	1	1.180	..	133.4	3	1.40	..	157.2	3	1.22	..
166.2	1	1.161	..	138.7	2	1.35	..	162.4	2	1.18	..
170.9	2	1.136	..	142.7	2	1.32	..	170.0	1	1.14	..
174.2	1	1.119	..	152.8	2	1.245	..	175.3	2	1.11	..
189.0	1	1.050	..	158.0	2	1.210	..	184.2	1	1.07	..
194.0	1	1.028	..	161.4	1	1.190	..	..	..	..	..
215.3	1	0.954	..	174.1	1	1.118	..	..	..	..	..
222.0	1	0.935	..	182.2	1	1.079	..	..	..	..	..
225.1	2	0.925	..	..	..	..	..	..	..	..	..

obtained—floated for 64 hours upon water at 38° C. containing aluminum powder in a paraffin-lined glass beaker. From this Formvar foil the patterns of Figure 5 were obtained.

Although there are clearly observable differences between the diffraction patterns of Figures 1 to 5, it is certain that they were produced by the same crystalline material. The

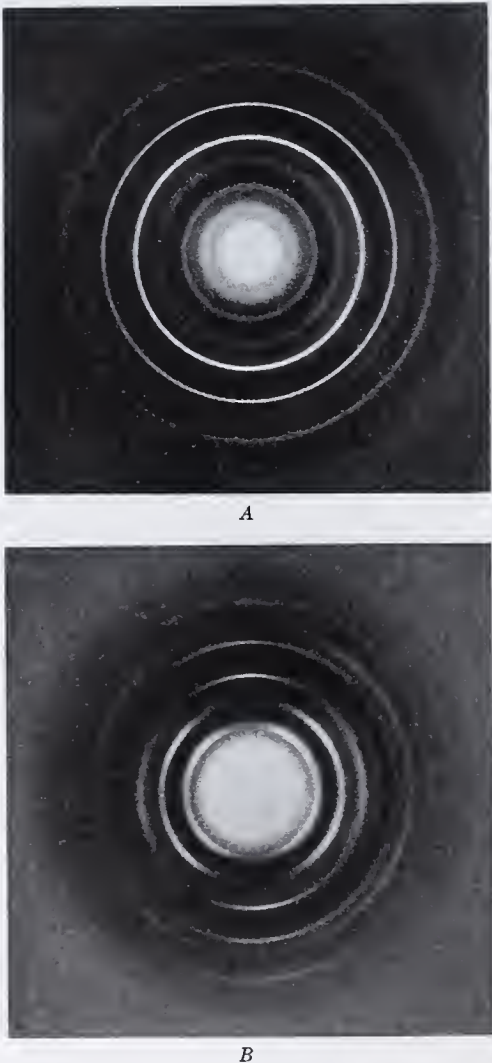


FIGURE 5. DIFFRACTION PATTERNS FROM FORMVAR FILM TREATED FOR 64 HOURS WITH ALUMINUM AND WATER AT 38° C.  
A. Normal incidence  
B. 45° incidence

differences between these patterns and their interpretations are discussed below.

Dr. Frary supplied x-ray diffraction photographs from three different hydrated oxides of aluminum—alpha-monohydrate (boehmite), beta-trihydrate (bayerite), and alpha-trihydrate (hydrargillite)—and with samples of the hydrated oxides themselves. The x-ray photographs were taken with unfiltered copper K radiation upon cylindrical films with specimen-film distances of 57.3 mm. The measured diameters and estimated intensities of diffraction rings upon these patterns are given in Table II, together with values of spacing  $d$ , calculated from the measured diameters by means of the Bragg formula. It is clear that some of the diffraction lines are due to copper K $\beta$  radiation, and these have been so designated; in some cases there is an uncertainty.

The calculated spacings and estimated intensities for aluminum alpha-monohydrate from Table II are written down again in the fourth and fifth columns of Table I. Comparison of these values with those from the electron diffraction pattern of Figure 1-A, indicates excellent agreement, except for the absence from the electron pattern of the reflection corresponding to 6.2 Å. which is extremely strong in the x-ray pattern, and for the presence in the electron pattern of a diffuse band of diameter 10.3 mm. and of a very weak ring of diameter 12.8 mm. The diffuse band is due to amorphous material which the authors have not identified, and the very weak ring is not found in other similar patterns. In view of the fact that the crystals examined by electron diffraction possessed considerable preferential orientation, while those examined by x-rays were randomly oriented, the absence from the electron pattern of the reflection corresponding to 6.2 Å. is not surprising.

Some of the dry powdered aluminum alpha-monohydrate, supplied by Dr. Frary, was ground in a mortar to make the particles extremely fine. This was dusted upon a well-polished chromium block, and a beam of electrons scattered from the surface at grazing incidence, yielding the diffraction pattern of Figure 6. In Table III are given measured radii and estimated intensities of rings of this pattern, and the corresponding crystal spacings calculated from the relation  $d = 2.345 \times 10^{-6}/R$  mm. These spacings and intensities are copied in the sixth and seventh columns of Table I.

It is clear that there is almost perfect agreement between x-ray and electron patterns from the powdered aluminum alpha-monohydrate, and that these patterns differ from those



from the authors' layers formed on silica films only in the absence from the latter of reflections corresponding to 6.2 Å. The material giving rise to the electron diffraction patterns of Figures 1 to 5 can be considered as definitely identified as aluminum alpha-monohydrate (boehmite).

As further matters bearing upon this identification, we need to account for the absence from the patterns of Figures 1 to 5 of the reflection corresponding to 6.2 Å. and to report the result of a spectroscopic examination of the film formed upon the surface of massive silica as a result of the reaction of aluminum and water at 38° C. The first of these matters, accounting for the absence of the 6.2 Å. reflection, is taken up below.

For the spectroscopic examination, a rod of fused quartz was soaked for some time in water at 38° C. containing aluminum powder. This rod was dried and brushed thoroughly to remove any loose material from its surface. A very small amount of material could then be scraped from the rod, and this was tested spectroscopically for aluminum and for silicon. Although the analysis showed traces of silicon, it was found that the amount of aluminum present was more than 200 times greater than the amount of silicon. This test proves that the film formed on the surface of the fused quartz rod was a compound containing aluminum but not silicon, in agreement with electron diffraction examinations of the material formed on the surface of amorphous silica films.

### Structural Characteristics of Monohydrate Layers

**THICKNESS AND CRYSTALLINE ORIENTATION.** The considerable crystalline orientation indicated by some of the diffraction patterns of Figures 1 to 5 is one of the most striking features of these patterns. The nature of the orientation is the same in all the monohydrate layers studied but its degree varies from zero to perfection, depending upon thickness of the layer and upon other factors.

The film that produced the diffraction pattern of Figure 2 at normal incidence gave a pattern at 45° incidence which is not reproduced here because it appears to be identical with Figure 2. The continuous circles of these patterns prove that the crystals were randomly oriented with respect to the film normal and with respect to a direction at 45° to it, and, since the film normal was the only unique direction, there must have been no preferential orientation of crystals at all.

The symmetry of Figures 1-A, 3, 4-A, and 5-A proves that in each of the corresponding films the crystals were randomly oriented about the normal to the film surface, but about other

directions the orientation was not random. Thus in each case the crystals tended to lie with some particular crystallographic plane parallel to the film surface, but were otherwise oriented entirely at random. If this orientation with a particular plane parallel to the surface were approximately perfect the diffraction patterns would differ from those of Figures 1, 4, and 5 in two obvious ways: The patterns at 45° would consist of sharply defined arcs, not lying upon weaker continuous circles; and in the patterns at normal incidence circles would appear corresponding to only those planes which belong to the zone defined by the normal to the film—that is, circles having the same diameters as the arcs along the vertical center lines in the patterns at 45°. These conditions are fulfilled for the pattern of Figure 3 and for one at 45° from the same film which is not reproduced; thus the orientation of crystals in this film was approximately perfect. In the other films, orientation, although marked, was extremely imperfect.

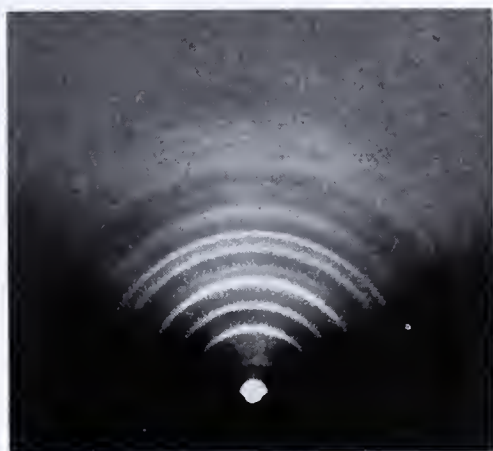


FIGURE 6. DIFFRACTION PATTERN FROM POWDERED ALUMINUM ALPHA-MONOHYDRATE BY REFLECTION METHOD

A film of silica treated with aluminum and water at 38° for a relatively short period of time (4 hours) gave a diffraction pattern essentially like that of Figure 3, indicating an unusually thin layer of monohydrate made up of perfectly oriented crystals. In monohydrate films deposited upon Formvar from peptized solution it has been found that crystals in very thin layers are almost perfectly oriented, in thick layers imperfectly, and in very thick layers random orientation has been found. There are, however, other factors beside thickness which influence degree of orientation, and these are not understood.

All the crystal planes which tend to lie normal to the film surface in the oriented layers, and which give reflections of observable intensity, have spacings which are inversely proportional to the square roots of the whole numbers 3, 5, 8, 12, and 20. These planes, designated by the numbers in the last column of Table I, were identified by the fact that in the patterns at 45° incidence reflections from them occur as arcs across the vertical center lines. The fact that these important planes, which belong to a common zone, have spacings related in this simple way may give a clue to the corresponding crystal structure, but the authors have not been able to follow it up.

**SIZES AND SHAPES OF CRYSTALS.** The major part of the widths of diffraction rings exhibited here is due to imperfect resolving power of the individual crystals, presumably on account of their limited size. That part of ring width at half maximum attributable to this cause,  $\Delta R$ , is related to the mean dimensions of contributing crystals normal to the primary beam,  $C$ , by the well-known Scherrer formula which, for

TABLE III. DATA FROM ELECTRON PATTERN OF ALUMINUM ALPHA-MONOHYDRATE

Measured Radii Mm.	(Figure 6) Estimated Intensities	Crystal Spacings Å.
3.7	4	6.3
7.3	7	3.21
10.0	6	2.34
11.5	1	2.04
12.5	7	1.88
13.1	2	1.79
14.0	3	1.67
15.1	1	1.55
16.2	5	1.45
16.8	1	1.40
17.8	5	1.32
20.0	2	1.172
20.6	3	1.155
22.5	2	1.042
25.8	3	0.909
27.1	2	0.856
28.2	3	0.832
29.2	1	0.803
30.3	1	0.774
35.2	1	0.666
38.2	1	0.614



the present experiments, can be written  $C = L\lambda/\Delta R = 2.3 \times 10^{-6}/\Delta R$  mm. This relation enables one to obtain information regarding mean size and shape of monohydrate crystals in many of the layers.

A surprising feature of Figure 1-A, is the fact that the rings corresponding to the whole numbers 3, 5, 8, and 12 are narrower and better defined than other rings. The authors believe that this must be attributed to lamellar shape of the crystals; the two sorts of rings are accounted for if each crystal, irrespective of its orientation, is thin in the direction of the zone axis of its "3, 5, 8, 12 planes" and relatively wide in directions at right angles to this axis. Although microphotometer curves of diffraction rings are necessary for reliable estimates of values of  $\Delta R$ , experience with a great many such curves (3) enables us to make fair estimates visually, and such visual estimates have been made for rings of Figure 1-A. These lead to 100 Å. as the average dimension of crystals in directions normal to the zone axis of its "3, 5, 8, 12" planes, and to 30 Å. as the average dimension in the direction of this axis.

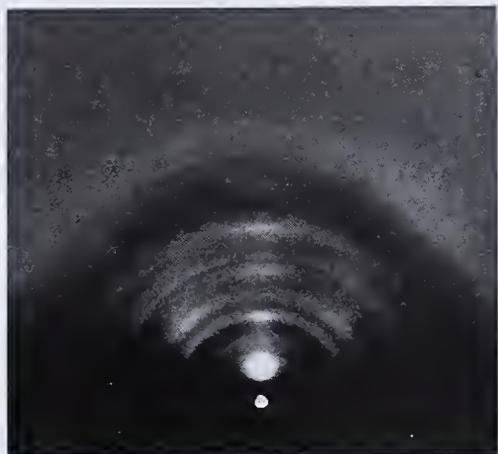


FIGURE 7. DIFFRACTION PATTERN FROM ALUMINUM HYDRATE PRECIPITATED UPON CHROMIUM BLOCK

Extremely thin layers of monohydrate (for example, the layer which produced the pattern of Figure 3) give, in general, patterns at normal incidence showing only the "3, 5, 8, 12 rings", and patterns at 45° incidence showing only short arcs having the diameters of these rings. From the shortness of these arcs in patterns at 45° incidence one can conclude that in these extremely thin layers the orientation is almost perfect, and from the absence of other arcs that the crystals are so thin normal to the film surface that they can scarcely be considered three-dimensional crystals at all.

The observations in this section, and in that immediately preceding, offer a fairly clear picture of the sizes, shapes, and orientations of monohydrate crystals in layers of various thicknesses. In very thin layers (probably less than 20 Å. or 30 Å.) the crystals are usually lamellar in shape, extremely thin, and lie almost perfectly flat upon a supporting silica or Formvar surface. In thicker layers the crystals are still lamellar in shape although not so extremely thin, and are more imperfectly oriented. In addition to thickness, some unknown factors influence shape and orientation of monohydrate crystals; crystals are sometimes randomly oriented, even in layers which are not extremely thick, and sometimes they are not lamellar in shape—for example, the layer which produced the pattern of Figure 2. These deductions regarding size, shape, and orientation of alpha-monohydrate crystals in layers of various thicknesses are consistent with facts already known about the crystallization of gelatinous alumi-

num hydrate, and they may be of interest in the chemistry of aluminum.

### Anomalies in Diffraction Patterns

MISSING REFLECTION CORRESPONDING TO 6.2 Å. The degree of orientation in the monohydrate layers which produced the patterns of Figures 1, 4, and 5 was so great that one would not expect reflections from the planes which tend to lie parallel to the film surface, even in patterns at 45° incidence. In other words, on account of crystal orientation the patterns of Figures 1-A, 4-A, and 5-A, must fail to contain reflections from at least one very important set of crystal planes, that normal to the "3, 5, 8, 12" zone axis. Yet all important reflections which appear on x-ray patterns from randomly oriented crystals are present in electron patterns at normal incidence, with the single exception of the reflection corresponding to 6.2 Å. If, then, the identification of aluminum alpha-monohydrate is correct, it is almost certain that the planes which tend to lie parallel to the film surface, normal to the "3, 5, 8, 12" zone axis, are separated by distances of 6.2 Å. The absence of reflections corresponding to 6.2 Å. seems thus to be accounted for on the basis of orientation.

This explanation is, however, inadequate. The crystals which produced the pattern of Figure 2 are known to be randomly oriented, but the pattern contains no ring corresponding to 6.2 Å., or any other ring not a part of patterns from oriented crystals. This is also true of other patterns from randomly oriented crystals. For example, an attempt was made to orient monohydrate crystals favorably for observation of the reflection corresponding to 6.2 Å. by submersion of a polished copper block for 24 hours in water containing aluminum powder at 38° C. The desired orientation of monohydrate crystals was not achieved, as a diffraction pattern obtained from this block by the reflection method was found to be characteristic of randomly oriented crystals of alpha-monohydrate. In this pattern, as in others from monohydrate layers prepared by adsorption from aluminum and water, no trace can be found of the reflection corresponding to 6.2 Å.

The anomaly of this missing reflection is not without precedent. Mongan (6) has reported that electron diffraction photographs from graphite powder do not contain reflections from the (002) basal plane which are the strongest reflections in x-ray patterns from graphite, and Trendelenburg (7) has found that graphite and a number of compounds which have structures of the layer lattice type often give electron patterns which do not contain reflections from the important basal planes. They attribute the absence of these reflections to lamellar shape of the crystals, which may perhaps be so broad parallel to the basal plane that electrons cannot go through them in this direction. It seems probable that a similar explanation must account also for the absence of reflections corresponding to 6.2 Å. from the monohydrate crystals, which are known likewise to have lamellar shapes in most cases. It is interesting to note again that the aluminum alpha-monohydrate powder, after grinding in a mortar, gave a diffraction pattern, Figure 6, in which a reflection corresponding to 6.3 Å. is clearly observed, although perhaps somewhat weak. We must conclude that grinding does not produce lamellar crystals, at least not such flat ones as are formed by precipitation from aluminum and water.

DIFFRACTION FEATURES NOT DUE TO ALPHA-MONOHYDRATE. In a further attempt to orient monohydrate crystals upon a massive block some of the authors' peptized solution of hydrated oxide was used. This was precipitated upon a block of highly polished chromium, and the diffraction pattern of Figure 7 obtained from it by the reflection method. There is no clear indication on this pattern of spots or rings



corresponding to 6.2 Å., the diffuse spots along the horizontal center line corresponding not to 6.2 Å., as might have been expected, but to 4.8 Å. This agrees (Table II) with the strongest diffraction ring from beta-trihydrate (bayerite) or from alpha-trihydrate (hydrargillite). Some of the other features of Figure 7 seem to be due to alpha-monohydrate, but many of them are not; all of the latter can be assigned satisfactorily to beta-trihydrate, although the data are by no means adequate to make the identification certain.

It is clear that layers of material precipitated from the peptized solution are, under some conditions at least, not entirely alpha-monohydrate. This has been observed in layers examined by the transmission method as well as those examined by reflection. For example, there are two diffraction rings on Figure 4-A, which cannot be assigned to alpha-monohydrate. These are a weak ring of diameter 9.5 mm. and a strong ring of diameter 11.0 mm., corresponding to 4.9 Å. and to 4.3 Å., respectively. The experiment described in the preceding paragraph and examination of Table II indicate that these may well be produced by a small amount of aluminum beta-trihydrate (or alpha-trihydrate). There is, however, no indication of the presence of trihydrate crystals in any of the patterns obtained, either by the reflection method or by the transmission method, from layers formed directly from metallic aluminum and water.

**INTENSITY ANOMALIES.** On account of the different degrees of orientation in various alpha-monohydrate layers one anticipates different relative intensities of rings. One does, however, expect to find that the relative intensities of rings due to planes of the "3, 5, 8, 12" zone will be the same in all patterns at normal incidence. Yet this is not true. It is obvious on the reproductions that these particular rings stand in order of relative intensity, from strong to weak, 3, 5, 8 in Figures 1-A and 5-A, but in the order 5, 3, 8 in Figures 3 and 4-A. How this can come about is not clear, but exactly the same phenomenon has been reported previously (4) in patterns from films of nickel hydroxide,  $\text{Ni}(\text{OH})_2$ .

### Miscellaneous Observations

**EXPERIMENTS IN BAKELITE BEAKERS.** Silica films are often greatly weakened or broken up by treatment with aluminum and water at 38° C. All the tests described thus far were carried out in paraffin-lined glass beakers. When similar tests were attempted in Bakelite beakers the rate of destruction of silica films was greatly increased, and no satisfactory experiments could be made. This destruction of films, which puzzled the authors for some time, was finally explained as due to the mechanical action of bubbles; these are produced by the reaction of aluminum and water, rise to the surface, and break floating films by striking them from below. In a paraffin-lined beaker most of the bubbles adhere to the surface of the paraffin and do not rise to the surface at all, but in a Bakelite beaker all bubbles rise. When a platinum baffle was placed in a Bakelite beaker in such a way that it protected a floating film from rising bubbles, the film lasted longer than in a paraffin-lined beaker without a baffle.

The authors succeeded in obtaining interesting diffraction patterns from silica films treated with aluminum and water in Bakelite beakers only when the films were protected from bombardment by bubbles. The patterns from these films are due to aluminum alpha-monohydrate. The rate of formation of aluminum hydrate on a silica film is, however, many times lower in a Bakelite beaker than under the same conditions in a paraffin-lined glass beaker. Dr. Frary has pointed out that this difference is probably due to adsorption of aluminum hydrate upon Bakelite surfaces but not upon paraffin surfaces, and consequent reduction of the concentration in Bakelite beakers but not in paraffin beakers.

**FORMATION OF SCUM.** Scum forms on water surfaces in beakers containing aluminum and water at 38° C. This scum develops much more rapidly in paraffin-lined beakers than in Bakelite beakers, and of course it does not develop at all in beakers containing silica and water without aluminum. The difference in the rate of formation of scum in paraffin and in Bakelite is consistent with the observation above, that aluminum hydrate is precipitated upon silica much more rapidly in a paraffin beaker than in a Bakelite beaker, and the difference appears to be accounted for by Dr. Frary's explanation. It seems clear that in the case of long reaction times, during which a great deal of hydrated alumina is formed, much of it appears as scum in a paraffin-lined beaker, but in a Bakelite beaker most of it adheres to Bakelite surfaces.

Many bits of scum have been caught upon Formvar foils for examination by electron diffraction. Scum from Bakelite beakers gives patterns which are readily identified as due to aluminum alpha-monohydrate. Some samples of scum from paraffin-lined beakers also give patterns identified as alpha-monohydrate, but others give patterns which are entirely different. A typical diffraction pattern of the latter sort is reproduced as Figure 8.

The patterns of Figure 9 were obtained under unusual conditions. A small piece of silica and a bit of scum were caught together upon a Formvar foil lying across the usual supporting slit. In the diffraction camera the electron beam could be adjusted so that it passed through the silica or through the scum; the former produced the pattern of Figure 9-A, and the latter that of Figure 9-B, which were recorded on the same photographic plate. The pattern from the silica film is clearly that of sharply oriented alpha-monohydrate crystals, while the pattern from the adjacent scum resembles that of Figure 8.

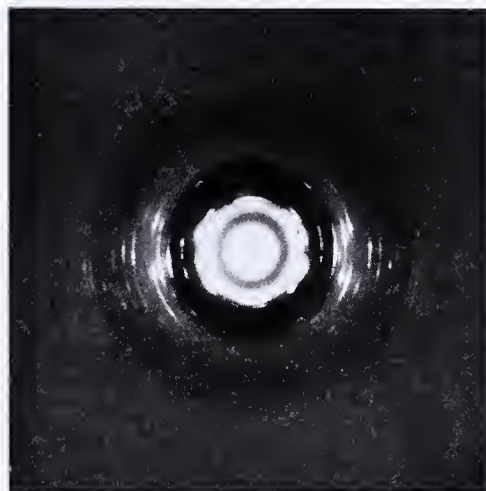


FIGURE 8. DIFFRACTION PATTERN FROM SCUM NOT MONOHYDRATE

Another diffraction pattern from this same type of scum, more satisfactory in some ways than the patterns of Figures 8 and 9-B, is reproduced as Figure 10. This pattern was obtained at normal incidence with the constant of the diffraction camera,  $L\lambda$ , adjusted to  $3.205 \times 10^{-6}$  sq. mm., whereas all other patterns which appear in this paper were obtained at  $L\lambda = 2.345 \times 10^{-6}$  sq. mm.

A clue to the structure of this type of scum is furnished by a rectangular array of diffraction spots which can be seen plainly in Figure 9-B, and less clearly in Figure 8. Whereas the material which produced the pattern of Figure 10 was polycrystalline, a considerable part of that giving the pattern of Figure 9-B (or Figure 8) made up a single crystal. The



fundamental rectangle of the arrays of spots in Figures 8 and 9-B, has sides of approximately 6.3 and 9.4 mm. Because of change in the constant of the camera a corresponding rectangle in Figure 10 would have sides equal to  $6.3 (3.205)/2.345 = 8.6$  mm. and  $9.4 (3.205)/2.345 = 12.8$  mm. It seems probable that the continuous rings of Figure 10 are generated by rotation of such a rectangular array of spots about the direction of the primary beam, and this is proved to be true by data relating to Figure 10 given in Table IV. In the first two columns are given measured diameters and estimated intensities of the rings of Figure 10, and in the last column all possible diameters up to 66.7 mm. as calculated from the relation  $D = (73h^2 + 164k^2)^{1/2}$  where  $h$  and  $k$  are any whole numbers. (In this expression 73 is approximately the square of 8.6, and 164 the square of 12.8.) The agreement between measured and calculated diameters is extremely good.

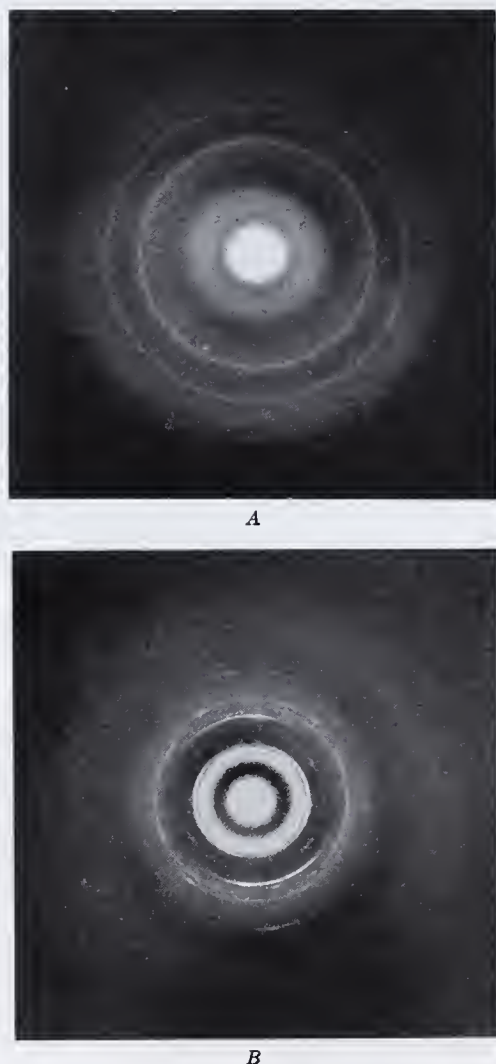


FIGURE 9. DIFFRACTION PATTERNS FROM SILICA AND FROM SCUM CAUGHT TOGETHER FROM A PARAFFIN-LINED BEAKER

A. Pattern from silica film. Monohydrate  
B. Pattern from scum. Not monohydrate

It is easy to show that the pattern of Figure 10, and also that of Figure 8 and of Figure 9-B, are due to crystals which are sharply oriented each with two of its crystal axes in the plane of the surface.

The lengths of the edges of the unit cell parallel to these axes are  $2(3.205 \times 10^{-6})/\sqrt{73} = 7.5 \times 10^{-7}$  mm. = 7.5 Å. and  $2(3.205 \times 10^{-6})/\sqrt{164} = 5.0 \times 10^{-7}$  mm. = 5.0 Å. (5). The product of these two lengths, 37.5 sq. Å., corresponds closely to the known cross-sectional area of two hydrocarbon chains. The complete absence of reflections for which values of the third Miller index can be determined suggests strongly that the length

TABLE IV. PATTERN FROM SCUM REPRODUCED AS FIGURE 10

Measured Diameters Mm.	Intensities	Calculated— Miller indices		Diameters, $\sqrt{73h^2 + 164k^2}$ Mm.
		$h$	$k$	
..	..	1	0	8.5
15.5	10	0	1	12.8
17.1	9	1	1	15.4
21.4	5	2	0	17.1
25.5	6	2	1	21.4
..	..	0	2	25.6
27.0	3	3	0	25.6
28.6	8	1	2	27.0
30.8	6	3	1	28.7
34.0	5	2	2	30.8
36.3	5	4	0	34.2
39.2	3	3	2	36.3
42.2	3	4	1	36.5
42.8	..	0	3	38.4
44.5	2	1	3	39.4
46.2	1	2	3	42.1
49.7	2	4	2	42.7
51.5	2	5	0	42.7
54.0	1	5	1	44.6
57.3	2	3	3	46.2
61.2	1	5	2	49.8
..	..	0	4	51.2
64.0	1	6	0	51.3
..	..	4	3	51.4
66.8	1	1	4	51.9
..	..	6	1	52.8
..	..	2	4	54.0
..	..	3	4	57.3
..	..	6	2	57.3
..	..	5	3	57.5
..	..	7	0	59.8
..	..	7	1	61.2
..	..	4	4	61.6
..	..	0	5	64.0
..	..	6	3	64.1
..	..	1	5	64.6
..	..	7	2	65.1
..	..	2	5	66.3
..	..	5	4	66.7

of the unit cell parallel to the third crystal axis is very great. That the structure is probably orthorhombic is indicated by the absence of reflections of the form  $(h0)$  for  $h$  odd, and of  $(0k)$  for  $k$  odd (see Table IV), and, as soon as the presence of long hydrocarbon chains is admitted, by the rather uniform intensity of the rings of Figure 10, and by the fact that the product of the edges  $a \times b = 37.5$  sq. Å. is equal to the known cross-sectional area of two hydrocarbon chains, rather than a larger value which it would have if the structure were monoclinic.

These considerations impel one to the inference that this type of scum is a soap of a long-chain organic acid and, since it does not appear in the absence of aluminum, is an aluminum soap. This conclusion is supported by the pattern of Figure 11 which was obtained at an incident angle of  $45^\circ$  from a sample of scum similar to that which at normal incidence gave the pattern of Figure 10. Except for diffuse rings from the supporting Formvar foil, the pattern of Figure 11 is made up entirely of arcs lying along lines separated by 13.8 mm. and parallel to the axis of rotation. This separation corresponds to a distance of  $2.345 \times 10^{-6} \sin 45^\circ / 13.8$  mm. = 2.4 Å. repeated normal to the film. The sharpness of the lines proves that this distance is either the length of the unit cell, or is a distance that is repeated many times within each unit cell. As only the latter hypothesis is plausible, the diffraction pattern of Figure 11 offers convincing proof that this type of scum is composed predominantly of long hydrocarbon chains. The difference between 2.4 Å. and the theoretical value of 2.52 Å. is probably attributable to inaccuracy in setting the incident angle of  $45^\circ$ .

Dr. Frary has suggested that the long-chain organic acid, which must be a constituent of this "soap" scum, comes from paraffin, and the authors' observations support this view. In the first place, the soap scum has never been found upon water in a Bakelite beaker. Furthermore, in a paraffin-lined glass beaker only a limited amount of scum is formed. Most of the visible scum was scraped from the beaker from which was obtained the material that gave the pattern of Figure 10, and the beaker was then allowed to stand at  $38^\circ$  C.



for an additional 90 hours; at the end of this time newly formed scum caught from the surface gave an excellent diffraction pattern characteristic of aluminum alpha-monohydrate, without any trace of features attributable to soap. It seems clear from these tests, and from others, that soap scum is formed only in paraffin-lined beakers and only initially, but that monohydrate scum continues to be formed indefinitely, probably as long as aluminum and water are present.

The experiment recorded in the patterns of Figure 9 indicates that, in the presence of monohydrate and of soap, the former is preferentially adsorbed upon silica. Other experiments, which confirm this assumption, are described in the following section.

**INFLUENCE OF PH.** In the first experiments there was no adjustment of pH of the distilled water which contained aluminum powder, but in later experiments pH was measured roughly and was regulated by the addition of hydrochloric acid or of potassium bicarbonate. Although the number of tests carried out with controlled pH has been undesirably small, some tentative generalizations can be drawn from them.

Scum that has been identified as soap has been obtained from water surfaces in paraffin-lined beakers at pH 4, 7.5, 8.5, and 9. It seems that soap can be formed at any value of

and water at 38° C. always gives diffraction patterns characteristic of aluminum alpha-monohydrate, without any trace of a pattern which could be attributed to soap. Silica treated with water and aluminum in a paraffin-lined beaker at 38° C. and pH 4 gives results which are quite different. Under these conditions no sharp diffraction pattern is obtained from a silica film in general. In one experiment, after a reaction time of 68 hours at pH 4, a very weak pattern characteristic of soap was obtained from a silica film.



FIGURE 11. PATTERN AT 45° INCIDENCE FROM LAYER OF SCUM

Similar to that which produced Figure 10  
 $\lambda\lambda = 2.345 \times 10^{-8}$  sq. mm.

Measured Diameters Mm.	Estimated Intensities (Arbitrary Scale)	Crystal Spacings Å.
11.3	9	4.15 <sup>a</sup>
13.2	4	3.55 <sup>a</sup>
18.9	1	2.48
21.2	1	2.21
22.7	6	2.06 <sup>a</sup>
24.5	1	1.91
26.5	2	1.77
31.1	1	1.51
33.0	1	1.42

<sup>a</sup> Due to planes belonging to zone that tends to lie normal to silica surface.

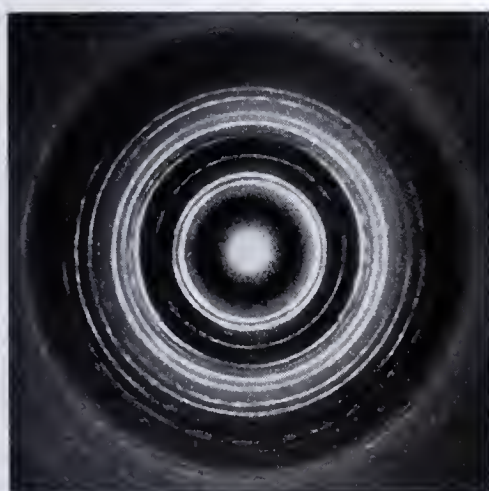


FIGURE 10. PATTERN AT NORMAL INCIDENCE FROM SCUM

$\lambda\lambda = 3.205 \times 10^{-8}$  sq. mm.

pH in this range. Monohydrate scum has been obtained from beakers at high values of pH, but never at low pH. At pH 4 monohydrate scum does not form at 38° C., or, if it does form, the authors have not discovered it.

At high and medium pH values (6.5 to 9) the material formed on silica films in contact with a mixture of aluminum

These observations can be summarized very briefly. At pH 4 only soap is formed, either as scum or upon silica, but upon silica it seems to form only with extreme slowness and not at all in some cases. At pH 6.5 to 9 only monohydrate is formed upon silica; in this pH range scum is either monohydrate or soap, but usually the former. Soap is not formed upon water surfaces in Bakelite beakers.

**EXPERIMENTS WITH COMMERCIAL ALUMINUM HYDROXIDE.** Denny, Robson, and Irwin (1) have reported that, whereas the solubility of silica in water is greatly reduced by the presence of aluminum powder, it is inappreciably changed by crystalline aluminum alpha-monohydrate or alpha-trihydrate. Because of this observed difference the authors have carried out experiments in which commercial aluminum hydroxide (Eimer & Amend c. p. grade) was used in place of aluminum powder.

Silica films were floated for 65 hours and for 140 hours upon water at 38° C. containing this hydroxide. Diffraction patterns obtained at normal incidence from these films contain sharp rings having the same diameters. The rings from the film which was treated for 160 hours are, however, extremely weak, and those produced by the other film are still weaker. Patterns obtained at incident angles of 45° contain well-defined arcs, proving that the crystals were rather well oriented upon the silica surface. From the extreme weakness of the diffraction features we can conclude that, although some oriented crystalline material was certainly deposited upon these films, the thickness of the layer was a great many times smaller than that of a layer of monohydrate which would have been formed in the same time if metallic aluminum had been used in place of the hydroxide. The failure of aluminum hydroxide (probably hydrargillite) to reduce the solubility of silica in water seems thus to be explained.

In Table V are given data from one of the patterns obtained at normal incidence. It is clear from comparisons of the spacings of the last column of Table V with those given in Table II that the material deposited upon silica in the pres-



ence of aluminum hydroxide is not aluminum alpha-monohydrate, alpha-trihydrate, or beta-trihydrate; and that it is not the soap for which data are given in Table IV. Attempts at identification have been made difficult by the extremely weak diffraction patterns available, and have not been successful.

### Interpretation

The experiments that have been described prove that the protective film formed on silica as a result of the reaction of aluminum and water is a hydrated oxide of aluminum which after thorough drying in the vacuum of the diffraction camera is crystalline aluminum alpha-monohydrate. Whether or not the film before drying can be properly described as alpha-monohydrate is an uncertainty which the diffraction experiments obviously offer no way of resolving.

There are, however, reasons for believing that the film is probably a highly hydrated gelatinous oxide which becomes crystalline only upon drying. One of these reasons is the fact that Denny, Robson, and Irwin (1) have discovered that the protective film formed on silica can be stained a deep pink by aurintricarboxylic acid; gelatinous aluminum hydrate is stained in this way, but crystalline alpha-monohydrate is not. They observe, furthermore, that activated amorphous alumina (colloidal) is almost as effective in reducing the solubility of silica in water as is metallic aluminum powder, whereas crystalline alpha-monohydrate is almost completely ineffective.

Transformation of amorphous gelatinous hydrated alumina into crystalline alpha-monohydrate upon drying agrees with the known behavior of hydrated oxides of aluminum. Fricke and Hüttig (2) state that boehmite (alpha-monohydrate) is the first product of the aging of amorphous aluminum hy-

droxide gel, being formed from it spontaneously in the cold. The aging of aluminum hydroxide gel at room temperature is said to proceed by way of boehmite and bayerite to hydrargillite. Amorphous gel can be obtained by precipitation from aluminum salt solution only if the operation is carried out rapidly and preferably at low temperature (0° C.). Otherwise a considerable amount of boehmite is obtained.

The authors' experiments have shown that aluminum hydrate is precipitated fairly rapidly upon silica at pH values lying within a range in which lie also the pH values of body fluids of men and of animals. Since in these experiments aluminum hydrate is not precipitated upon silica at pH 4, it seems highly probable that aluminum would not afford protection from silicosis to a hypothetical animal with body fluids of pH 4.

### Acknowledgment

The authors are greatly indebted to Dr. Frary for proposing the problem of the identification of the protective film on silica particles, for his continued interest throughout the course of the work, and for a very great amount of assistance and advice over a period of many weeks.

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## A Substitute for Laboratory Oil Baths

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THE many difficulties—fumes at high temperatures, spattering from drops of water, messiness from spilling, greasiness on bottoms of flasks, deterioration of oil, etc.—inherent in use of oil baths have prompted replacing them with aluminum pots for air baths. The substitutions have proved such a decided improvement that this mention is warranted.

Special features in construction are (1) thick sides and bottom, which permit drilling thermometer wells in the metal and provide enough heat capacity to keep the temperature reasonably constant for hours at a time; (2) a considerable depth, so that the whole flask and part of the neck can be covered. The depth makes it possible to heat as little or as much of the flask as desired, to cut out a section through which a side arm can protrude so that high-boiling distillates can be kept hot until they reach the receiver, or to use the pots for small furnaces in which short tubes or bottles can be heated. Holes can also be drilled through the bottom or side of a pot as needed for any special furnace construction and subsequently plugged with asbestos without interfering seriously with normal use. The relatively light weight permits suspending many of the pots by their rims in the ordinary iron ring. They can also be supported on their sides or upside down—variations in positions which are sometimes desirable for sublimations, distillations from a horizontal position, or

other special operations. Such a degree of usefulness cannot be attained with an oil bath.

It has been found convenient to have pots of different sizes, with about a 3-mm. clearance between the wall and standard-size flasks. This arrangement permits heat to enter through the side of the flask as well as the bottom, so that in distillations there is less tendency for bumping. Asbestos can be placed in the bottoms in order to reduce further the amount of heat from that direction. For molecular distillations with the Hickman alembic or other special apparatus, a closely fitting casting with a slot cut for the low side arm permits a very even heating without necessity of electrical wiring and special insulation which is apt to become loose after repeated handling by a class of students.

The following inside dimensions were found convenient for use with ordinary flasks: 1-liter flask, 14-cm. diameter by 15.5 cm. deep, weight 3.7 kg.; 500-ml. flask, 10.8-cm. diameter by 15.3 cm. deep, weight 2.7 kg.; 300-ml. flask, 9.5-cm. diameter by 19.2 cm. deep, weight 2.9 kg.; 100-ml. flask, 6.9-cm. diameter by 19.6 cm. deep, weight 2 kg.; 50-ml. flask, 5-cm. diameter by 15.4 cm. deep, weight 1.4 kg. Usually the large sizes were made less deep in order to reduce the weight. In all cases the walls and bottom were 1.3 cm. thick. A rim 6 mm. thick and projecting 12 mm. beyond the pot at the top made a convenient grip and support.

Castings were made by S. C. Bockman, 244 Sixth St., Cambridge, Mass.



# Tentative Procedures for Testing the Variability of Normal and Concentrated Latex

Crude Rubber Committee, Division of Rubber Chemistry, American Chemical Society, R. H. Gerke, Chairman,  
U. S. Rubber Products, Inc., Passaic, N. J.

THE committee desires to emphasize that these tentative procedures for testing variability are not to be considered as actual specifications for buying or selling latex, since tolerances or limits are not given. Rather, it is the desire of the committee to give what are believed to be reliable methods for the determination of the various properties of latex which have been listed. However, it may be necessary to revise some of these procedures from time to time, since the use of latex is in its infancy and improved methods are being rapidly developed. In listing these procedures the committee does not mean to suggest that it is always necessary to use all of them in testing a sample of latex. In other words, it is up to the users and suppliers to select such methods and tolerances as they see fit, which will best suit their purposes.

The committee desires to express deep appreciation to those who have been instrumental in preparing the attached procedures:

W. A. Davey, Rubber Research Institute of Malaya  
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## Sampling Latex<sup>1</sup>

1. LATEX IN DRUMS, L-1a. *Outline.* The contents of the drum are thoroughly mixed and the sample is removed by means of a sample bottle.

*Details.* In case the sampling operation takes place immediately after the drum is filled, no further mixing is required. In case the drum has stood, the top should be removed and the contents stirred with a high-speed stirrer for 10 minutes.

Attach a 1-liter (32-ounce) open bottle to a 120-cm. (4-foot) length of 0.625-cm. (0.25-inch) steel rod. Introduce the bottle thus attached to the rod into the drum and run it down through the entire body of latex. Withdraw the bottle, discard the contents, refill the bottle, and stopper tightly. This double filling eliminates the possibility of diluting the sample with water which may be present initially in the bottle. It will be found advantageous to leave a small air space in the top of the bottle after the second filling in order to facilitate mixing before weighing out samples.

If closed-head drums are used, a procedure of rolling and up ending the drums must be resorted to. Rolling alone is not sufficient. If there is a free air space in the drum, satisfactory mixing can be accomplished within a short time by this means. In case of full drums, transfer all the latex in the closed-head drum

to a larger vessel and then take sample according to either of the above procedures.

2. LATEX IN TANK CARS, L-1b. *Outline.* The contents of the car are thoroughly mixed and a sample is obtained by introducing a 1-liter (1-quart) sample bottle attached to a 300-cm. (10-foot) length of 0.625-cm. (0.25-inch) steel rod.

*Details.* In case the tank car has been freshly filled, no further mixing will be necessary. If the car has stood, it will be necessary to mix the latex by means of a jet of air from a 1.25-cm. (0.5-inch) pipe inserted through the dome cover of the car and moved continuously throughout the body of the latex. In the case of normal latex, this operation should be continued for 15 minutes, and in the case of creamed or centrifuged latex it should be continued for about 45 minutes.

When the contents of the car have been thoroughly mixed, introduce a 1-liter (32-ounce) narrow-mouthed sample bottle attached to a 300-cm. (10-foot) length of steel rod. Withdraw the bottle and empty the contents back into the car. This initial filling minimizes the possibility of errors from moisture which may be in the bottle. Next, force the bottle quickly down through the body of the latex and raise and lower it rapidly through the entire depth of the tank car several times. On account of the narrow mouth, there will be time to do this during the period of filling of the bottle. Withdraw the bottle when it is completely filled. Pour out just enough latex to leave a small air space in the top and stopper tightly.

## Determining Total Solids, L-2

*OUTLINE.* A weighed sample of latex is dried down for a given length of time under specified conditions of temperature. The film is then weighed and the result of the determination is expressed as percentage of total solids based on the whole original latex.

*DETAILS.* Weigh out  $2.5 \pm 0.5$  grams of the latex to be tested into a covered tinned ointment can or small covered dish which has been tared. The latex should be uniformly distributed over the bottom of the dish during drying. The area of the latex should be approximately 32 sq. cm. (5 square inches). Remove the cover and dry the sample in air for 16 hours at 70° C. The percentage of total solids may be calculated by means of the following equation:

$$\text{Percentage of total solids} = \frac{100 \times \text{weight of dried film}}{\text{weight of latex sample}}$$

## Determining Dry Rubber Content, L-3

*OUTLINE.* A weighed sample of latex is coagulated with acid, then washed and dried at an elevated temperature. The result is expressed as percentage of dry rubber content based on the whole original latex.

*DETAILS.* Weigh out into a porcelain evaporating dish a representative sample of not less than 20 grams of normal latex or 10 grams of concentrated latex and add distilled water until the total solids content is approximately 25 per cent. To this add 2.0 per cent acetic acid solution with stirring until the latex appears to be coagulated and more acid produces no effect. Place the dish on a steam bath and leave for 0.5 hour. Pour off the serum and replace with distilled water. Remove the coagulum and pass between the tightly closed rolls of a laundry wringer or similar device; then wash again with distilled water and wring out. Repeat this process five times. Dry the resulting crepe to constant weight at 70° C. Calculate the dry rubber content as follows:

$$\text{Dry rubber content} = \frac{\text{weight of dry coagulum} \times 100}{\text{weight of sample}}$$

<sup>1</sup> The procedure for sampling latex is given as an example, and may obviously be altered in certain details.



### Determining Coagulum, L-4

**OUTLINE.** A weighed sample of latex is filtered and the coagulum remaining on the filter is washed and dried. The result is expressed as percentage of coagulum based on total solids.

**DETAILS.** A steel pipe union of about 3.75 cm. (1.5-inch) inside diameter is fitted with a one-hole stopper into a suction flask. Between the two parts of the union, a tared circular section of 80-mesh stainless steel screen is inserted so that when the union is screwed together this screen is held firmly in place.

In order to determine coagulum, weigh out 200 grams of latex from a well-stirred sample and dilute with an equal volume of 5 per cent alkali soft soap solution. Sodium or potassium oleates are recommended. Filter this mixture through the 80-mesh sieve in the steel union and wash the coagulum remaining on the filter with 5 per cent soap solution. Finally wash the coagulum free of soap with distilled water. Remove the screen from the union and dry to constant weight at 70° C. The difference in weight of the screen and the weight of the screen plus coagulum held back represents the weight of dried coagulum. Calculate the percentage of coagulum as follows:

$$\text{Percentage of coagulum} = \frac{10,000 \times \text{weight of dried coagulum}}{\text{weight of latex sample} \times \text{percentage of total solids}}$$

### Determining Methyl Red Titer or Alkalinity

1. **LATEX CONTAINING NO FIXED ALKALI OR BASE OTHER THAN AMMONIA, L-5a.** *Outline.* The ammonia in a weighed sample of latex is titrated directly with a standard acid solution, using methyl red as an indicator. The result is expressed as percentage of dry ammonia (NH<sub>3</sub>) based on the whole original latex. (The precision of this method is affected by the presence of phosphates and proteins in the latex, which may lead to apparent ammonia contents as much as 0.05 per cent too high based on the weight of the sample.)

*Details.* Pour approximately 10 cc. of the latex into a tared weighing bottle. Immediately cover the bottle. Weigh it to ±0.05 gram. Place 300 cc. of distilled water in a 600-cc. beaker. Uncover the weighing bottle and immediately immerse it in the water in the beaker. Stir the solution thoroughly with a glass rod. Add 6 drops of a 0.1 per cent alcoholic solution of methyl red and titrate with approximately 0.1 N standard acid until the indicator becomes pink. The end point occurs before complete coagulation takes place and the color change of the indicator can be detected against the white background of the slightly curdy latex. High results will be obtained if the addition of acid is continued until complete coagulation occurs. The calculation is carried out as follows:

Let  $w$  = the weight of the sample of the latex

$N$  = the normality of standard acid

$n$  = the number of cc. of standard acid necessary to neutralize the ammonia

$$\text{Then the percentage of ammonia} = 1.7 \frac{(N \times n)}{(w)}$$

**PRECAUTION.** In a direct titration of latex with acid, the acid should not be added so rapidly as to produce local coagulation. Continuous stirring and a moderate rate of addition of the acid are recommended to avoid this.

2. **PROCEDURE FOR TOTAL AMMONIA CONTENT, L-5b.** *Outline.* The ammonia is distilled from a weighed sample of latex, to which has been added an excess of magnesium oxide, into a measured quantity of standard acid. The excess acid is back-titrated with standard alkali solution.

*Details.* Weigh out 10 cc. of latex, dilute with water to about 250 cc., and add 4 grams of magnesium oxide. From this mixture distill about 100 cc. into 0.1 N sulfuric acid, the amount of the latter exceeding by about 10 cc. the amount used for the determination of the alkalinity. Boil the distillate for 2 minutes and after cooling determine the excess of sulfuric acid by titration with 0.1 N alkali, using methyl red as an indicator.

### Determining pH in Latex, L-6

It is recommended that anyone about to undertake the making of measurements of pH without having had previous experience in

the use of electrometric apparatus should consult Clark's book (2) in order to familiarize himself with the general technique.

**OUTLINE.** The only suitable means for the accurate determination of pH in latex is the glass electrode.<sup>2</sup> It may be used in conjunction with any one of the various potentiometric arrangements commercially available. In order to make a measurement of pH, the glass electrode is dipped into the solution under test and suitably connected to the reference half-cell and potentiometer. The potentiometer is then balanced, and by means of equations detailed below the potentiometer reading is converted to pH units.

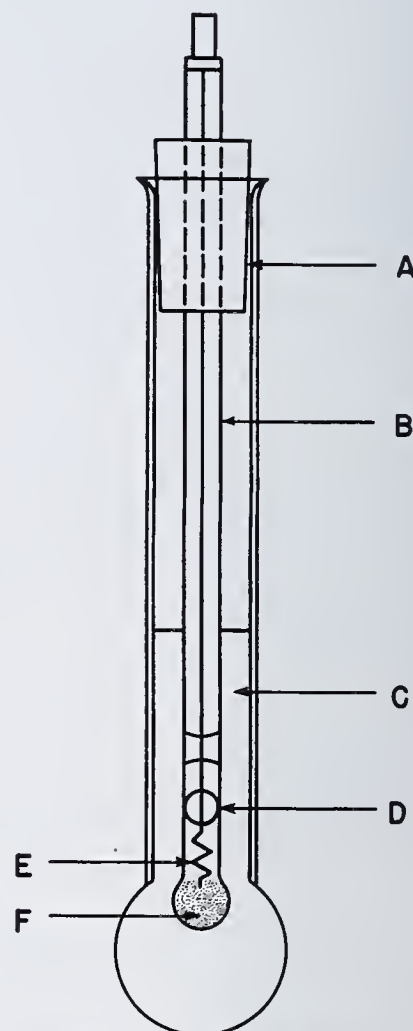


FIGURE 1. GLASS ELECTRODE ASSEMBLY

- A. Rubber stopper
- B. Inner electrode
- C. Hydrochloric acid solution at pH 1
- D. Opening for introduction of quinhydrone
- E. Platinum electrode
- F. Quinhydrone

**DETAILS. Description and Use of Glass Electrode.** There are two types of auxiliary apparatus which may be satisfactorily used with the glass electrode: (1) a standard battery circuit with a student-type potentiometer and a reflecting galvanometer of sufficient sensitivity; (2) a battery circuit with a vacuum-tube galvanometer. Several instruments of the vacuum-tube type are commercially available, some of which require a separate potentiometer and some of which are completely self-contained. For details of preparation and maintenance of glass electrodes and auxiliary apparatus reference must be made to the pamphlets and circulars describing the various individual types of apparatus.

An essential part of the glass electrode is always a thin shell blown on the end of a glass tube of specific composition. This shell contains a standard reference electrode, usually of quinhydrone in a solution of unit pH. When an individual shell has

<sup>2</sup> The reasons for restricting the specification to the use of the glass electrode have been discussed in detail by Jordan, Brass, and Roe (5).



once been prepared for use, it must be calibrated with the help of standard buffer solutions, the pH of which has been determined by means of the hydrogen electrode. When the electrode has been suitably calibrated (detailed directions are to be found below), it is ready for use.

In order to measure the pH of an unknown solution, bring the solution to be tested to a temperature of 25° C. or to the operating temperature which prevails in the control test. (A water thermostat kept at this temperature should be available. The calomel reference electrode and the potassium chloride bridge solution should be suitably immersed in this thermostat.) Insert the glass electrode in the test solution so that the bulb is completely immersed, and make the usual electrical connections, including the introduction of a salt bridge between the test solution and the beaker containing the saturated potassium chloride bridge solution, if a separate calomel electrode is used. Balance the potentiometer with respect to the standard cell in accordance with the directions to be found in (4) or in the pamphlets of directions provided with special forms of apparatus. When this has been done, replace the standard cell by the glass electrode cell and balance the potentiometer against the latter. The potentiometer reading so obtained may be in terms of volts or directly in pH units depending on the type of apparatus employed. If it is obtained in terms of volts, the reading may be converted into pH units by means of the following equation:

pH = A(E - E<sub>0</sub>) (1)

where E is the observed potential in volts of the glass electrode-calomel electrode cell as read on the potentiometer, and A and E<sub>0</sub> are constants for any given electrode at a constant temperature.

If the reading is directly in terms of pH units, no such conversion is required, but a calibration curve of the individual electrode should always be obtained and the corrections to scale readings should be utilized in testing unknown samples.

The determination of numerical values for these constants constitutes the calibration of any particular electrode and is described in the next section. When these numerical values are known, pH values may be calculated directly from the potentiometer readings by means of Equation 1.

**Calibration of Glass Electrode.** Prepare two standard buffer solutions as follows:

- 1. Add 50 ml. of 1 N potassium hydroxide solution to 50 ml. of 2 N acetic acid solution and make up with distilled water to 500 ml.
- 2. Dissolve 10 grams of anhydrous potassium bicarbonate in water, add 50 ml. of 1 N potassium hydroxide solution, and make up with distilled water to 500 ml.

It is essential to use potassium hydroxide rather than sodium hydroxide in preparing these buffers, since the glass electrode gives incorrect values in solutions containing sodium ions above a pH of 10. Determine the numerical pH values of solutions 1 and 2 by means of the hydrogen gas electrode in accordance with directions to be found in (3). (If sodium hydroxide could be used the hydrogen electrode standardization could be avoided since it is easily possible to obtain carbonate-free sodium hydroxide. However, it is much more difficult to obtain carbonate-free potassium hydroxide, and hence the hydrogen electrode standardization cannot be avoided.) When these buffers have been prepared and standardized, the next step is to find the value of the potential of the glass electrode cell when the glass electrode is immersed in each of the standard buffers.

- Let
- pH<sub>1</sub> = pH of standard buffer solution 1 as determined by the hydrogen electrode
  - pH<sub>2</sub> = pH of standard buffer solution 2 as determined by the hydrogen electrode
  - E<sub>1</sub> = glass electrode potential in standard buffer solution 1
  - E<sub>2</sub> = glass electrode potential in standard buffer solution 2
- Then from Equation 1

pH<sub>1</sub> = A(E<sub>1</sub> - E<sub>0</sub>)  
pH<sub>2</sub> = A(E<sub>2</sub> - E<sub>0</sub>) (2)

By solution of the simultaneous system 2 in A and E<sub>0</sub>, the following results are obtained:

A = (pH<sub>1</sub> - pH<sub>2</sub>) / (E<sub>1</sub> - E<sub>2</sub>) (3a)

E<sub>0</sub> = (pH<sub>1</sub>(E<sub>1</sub> - E<sub>2</sub>) / (pH<sub>1</sub> - pH<sub>2</sub>) (3b)

If the standard buffer solutions are protected from atmospheric contamination, they will not change in pH appreciably over a period of several months. Hence, the hydrogen electrode standardization need only be repeated at intervals of, say, one month. However, the calibration of the glass electrode should be repeated at frequent intervals; daily, if the glass electrode is in steady use. The aging characteristics of glass electrode shells vary somewhat from shell to shell, and consequently frequent checking of each individual electrode is absolutely essential.

**Precautions.** On account of the high electrical resistance of the glass electrode and the susceptibility of vacuum-tube galvanometers to external electromagnetic disturbances, special precautions are frequently required to shield the glass electrode outfit from such external disturbances.

If a vacuum-tube galvanometer is used, it has been found advisable to place the water thermostat together with the calomel and glass electrode half-cells within a metal jacket which can be completely closed while the potentiometer is being balanced. This metal jacket and the one side of the potentiometer should be grounded, and the electrical connections to the ungrounded side of the potentiometer should be as short as practicable. If an ordinary battery circuit is used in conjunction with the potentiometer, the galvanometer should be protected from stray sources of e. m. f. by grounding one terminal of the galvanometer and shielding it by means of a moisture-proof box. Frequent testing of the glass electrode in the standard buffers will serve as a check on the presence of external disturbances in the electric circuit. A variation of more than 10 millivolts in the glass electrode potential of either of the standard buffers, provided the buffers themselves have not changed (a point which should be checked with the hydrogen electrode) is an indication of difficulties with the electrical system.

The glass electrode fails in solutions of high pH containing sodium ions; hence, it is impossible to determine pH with the glass electrode in latices stabilized with sodium hydroxide.

When the glass electrode is used in latex, it should always be washed free of latex as soon as the determination is finished; otherwise coagulation may take place on the fragile glass mem-

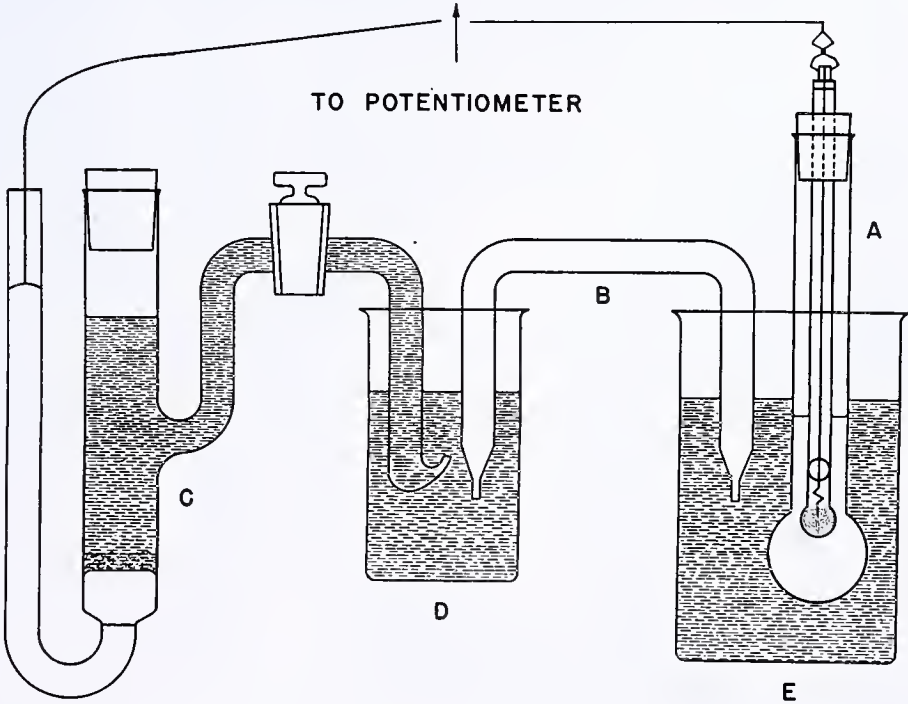


FIGURE 2. GLASS ELECTRODE-CALOMEL ELECTRODE ASSEMBLY FOR USE WITH APPARATUS NOT COMPLETELY SELF-CONTAINED

- A. Glass electrode
- B. Agar agar saturated potassium chloride bridge
- C. Saturated calomel electrode
- D. Beaker containing saturated potassium chloride solution
- E. Beaker containing solution under test



brane. In case a light skin of coagulum does form, it may be removed by rubbing the bulb with a soft wet brush.

### Determining Viscosity and Yield Point of Latices, L-7

**OUTLINE.** Two methods have been found satisfactory for the determination of viscosity and yield point of latex—namely, the capillary flow method and the rotating conical viscometer method. The former is advantageous on account of its simplicity and on account of the fact that the apparatus may be constructed from materials stocked in the laboratory. When the capillary viscometer is made in accordance with dimensions hereinafter specified, it is perfectly adapted to the measurement of viscosities of normal and concentrated latex up to 60 per cent total solids. In general, this instrument has the further advantage that results may be obtained in absolute units from a knowledge of the dimensions of the instrument and without recourse to calibration with a liquid of known viscosity. The rotating cylinder viscometer is rather expensive on account of details of its construction. However, this instrument has a wider range of applicability in dealing with latex than is possessed by the capillary flow apparatus and is in addition, from the theoretical point of view, the most satisfactory method of measuring the viscosities of non-Newtonian liquids like latex. In particular, the rotating cylinder viscometer may be used to measure the viscosities of high-solids latex material like Revertex. A description of this instrument is given by Mooney and Ewart (6). Specifications will be confined to the capillary flow method.

The capillary flow method consists of measuring the rate of efflux of the liquid to be tested through a capillary tube of known length and known radius under two known pressure heads. The limiting coefficient of viscosity, which is defined explicitly in a later section, is calculated from these data and is expressed in centipoises at 25° C. The yield value is expressed in grams per square centimeter.

**EXPERIMENTAL DETAILS.**  
**Apparatus.** The apparatus is pictured in Figure 3. It consists of two parts: a glass tube 80 cm. long and 1.2 cm. in inside diameter, and a capillary glass tube 10 cm. long and of known internal radius. Capillary tubes of different radii are specified for differing materials. On the large glass tube the marks  $M_1$ ,  $M_2$ ,  $M_3$ , and  $M_4$ , as shown in Figure 3, are so placed that the volume included between  $M_1$  and  $M_2$  is  $10 \pm 0.05$  cc. An equal volume is included between  $M_3$  and  $M_4$ . The mid-points of the intervals  $M_1M_2$  and  $M_3M_4$  should be separated by a distance of 35 cm. The capillary tube is inserted in the lower end of the 80-cm. cylinder by means of a one-hole stopper. It should be adjusted so that the upper end of the capillary is at a distance of 20 cm. below the mid-point of section  $M_3M_4$  and 55 cm. below the mid-point of section  $M_1M_2$ .

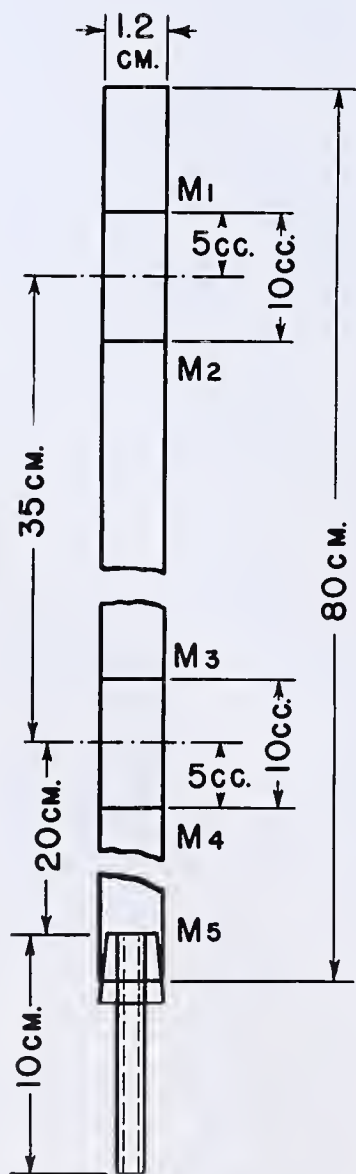


FIGURE 3. VISCOSITY APPARATUS

**Procedure for Determining Viscosity and Yield Point.** Assemble the glass tubes precisely as shown in Figure 3 and as described in the preceding paragraph. Hold one finger over the lower end of the capillary and fill the tube with latex to a point about 5 cm. above  $M_1$ . Place a beaker under the lower end of the capillary and allow the latex to run out through the capillary. By means of a stop watch determine to the nearest tenth of a second the time required for the meniscus to pass through the interval in the 80-cm. tube bounded by marks  $M_1$  and  $M_2$ . Similarly determine the time occupied by the meniscus in passing from  $M_3$  to  $M_4$ . If difficulty is experienced in seeing the meniscus, a small flash light placed behind the tube will be found helpful. Measure the temperature of the latex to the nearest 0.5° C. just prior to conducting the viscosity determination. During the passage of the meniscus from  $M_3$  to  $M_4$ , efflux from the capillary may take place dropwise. This is undesirable and can be prevented by bringing the lower end of the capillary nearly into contact with the latex in the receiving beaker.

**Calibration of Capillary.** Clean the capillary with chromic acid solution, wash with distilled water, and finally dry; then clamp the capillary in a nearly horizontal position and slowly pipet clean mercury into the upper end until it just flows out at the lower end. Scrape off the protruding meniscus by means of a spatula which is then held tightly against the capillary, and withdraw the pipet so that the capillary is completely filled with mercury. Likewise scrape off the meniscus protruding from the upper end. Empty the mercury contained in the capillary into a weighing bottle and weigh. Duplicate determinations should agree to 0.1 per cent. Determine the length of the capillary by means of a caliper or traveling microscope to the nearest 0.1 cm. Then, if

$R$  = radius of capillary in centimeters

$L$  = length of capillary in centimeters

$W$  = weight of mercury contained when the capillary is full

$D$  = density of mercury at temperature of measurement

the equation giving the radius is

$$R = \sqrt{\frac{WL}{\pi D}}$$

It is of great importance that the capillary be of uniform bore throughout its length. This can be checked up as follows with the aid of a microscope with a traveling stage. Place enough mercury in the clean capillary to fill it about half full. Measure the length of the mercury column in a random position in the tube by means of the microscope. Then tilt the tube so as to shift the position of the column of mercury to another section of the tube, taking care not to lose any mercury, and again measure its length. Repeat this several times. The length of the thread of mercury should not vary from place to place by more than 0.1 per cent.

**Preparation of Latex for Viscosity Measurement.** All viscosity measurements on concentrated latices should be made at 60 per cent total solids and on normal latices at 35 per cent total solids. After the adjustment of the total solids content, prepare the latex for a viscosity measurement by straining it through a 200-mesh silk sieve and deaerating it overnight. In case partial creaming takes place during the deaeration process, gently swirl the container while the latex is under reduced pressure to stir in this cream. Care should be taken that no bubbles are formed.

Types of Capillary for Use with Normal and Concentrated Latices

Type of Latex	Radius of Capillary Cm.
Normal	0.040 $\pm$ 0.002
Concentrated, 60%	0.070 $\pm$ 0.004

**Calculations.** In terms of Figure 3, let

- $t_1$  and  $t_2$  = times in seconds for meniscus to pass through intervals  $M_1M_2$  and  $M_3M_4$ , respectively
- $h_1$  and  $h_2$  = heights in centimeters of mid-points of intervals  $M_1M_2$  and  $M_3M_4$ , above bottom of capillary
- $d$  = density of latex in grams per cc.
- $R$  = radius of capillary in centimeters
- $L$  = length of capillary in centimeters
- $V$  = volume in cc. of each of the two intervals  $M_1M_2$  and  $M_3M_4$
- $g$  = acceleration of gravity in centimeters per second per second
- $T$  = temperatures in °C.
- $\eta_T$  = coefficient of viscosity in centipoises at  $T^\circ$  C.
- $\eta'_T$  = limiting coefficient of viscosity in centipoises at  $T^\circ$  C.
- $\eta$  = coefficient of viscosity in centipoises at 25° C.
- $\eta'$  = limiting coefficient of viscosity in centipoises at 25° C.
- $F_0$  = yield point at  $T^\circ$  C. in grams per square centimeter



For purposes of latex testing and control the limiting coefficient of viscosity  $\eta'$  is of more importance than the true coefficient of viscosity,  $\eta$ . In fact, the quantities  $\eta'$  and  $F_0$  completely specify the flow behavior of the latex in the range of practical interest for many purposes. Expressions for the calculation of  $\eta'$  and  $F_0$  are given at this point.

$$\eta'_{\tau} = K_1 \frac{t_1 t_2}{t_2 - t_1}$$

where

$$K_1 = \frac{\pi R^4 g d (h_2 - h_1) \times 100}{8 L V} \tag{1}$$
$$\eta' = \eta'_{\tau} [1 - 0.02 (25 - T)] \tag{2}$$
$$F_0 = K_2 - K_3 \frac{\eta'_{\tau}}{t_2} \tag{3}$$

where

$$K_2 = \frac{h_2 R d}{2 L}; K_3 = \frac{V}{25 \pi R^3 g}$$

*Note.* The reason for introducing the limiting coefficient of viscosity,  $\eta'$ , is that it is a constant for a given liquid of the latex type, whereas the true coefficient of viscosity is not. The introduction of the yield point,  $F_0$ , in the present sense and of  $\eta'$  is based upon the treatment of latex as an ideal plastic material in the sense of Bingham. This is not a true picture of the situation, but it is a sufficiently good approximation. A theoretical discussion of the behavior of such plastic bodies in the capillary viscometer is given by Bingham (1).

Laying Down Film of Rubber from Latex, L-8

**OUTLINE.** The purpose of specifying the manner of preparing a dried-down film of latex rubber is to obtain a material which can be directly subjected to the usual procedures for determination of manganese, copper, and acetone extract. A sheet of latex is spread onto a flat horizontal surface and slowly dried down to a transparent film by means of a current of warm air.

**DETAILS.** Spread the latex to be dried down on a glass plate. Convenient amounts to use will be 1 cc. of normal latex per 6.45 sq. cm. (1 sq. in.) of surface or 0.5 cc. of concentrated latex per 6.45 sq. cm. If the film is to be used to determine acetone extract, carry out the drying process in a current of warm air, the temperature of which should not exceed 35° C. The length of time necessary to complete drying varies with different latices and with external conditions. Experience will indicate safe limits in practice.

It is advisable during the drying process to protect the film from contamination with atmospheric dirt. For this purpose it may be found convenient to use a jet of air which has been filtered through glass wool.

Determining Copper and Manganese, L-9 and L-10

These determinations are carried out on samples of dried-down film in exactly the same manner as directed in the Crude Rubber Committee's specifications for rubber.

Inadvertently the procedures for copper and manganese have not been published. (The abridged reports of the Crude Rubber Committee, which will include the procedures for copper and manganese, will be published shortly in *Rubber Chemistry and Technology*.) The Crude Rubber Committee is cooperating with Sub-Committee XI of Committee D-11 of the American Society for Testing Materials, which has adopted these procedures as tentative but is planning certain revisions at the present time.

Determining Water-Solubles, L-11

**OUTLINE.** The procedure is to coagulate the ammonia-free latex with dilute acid and then to determine the water-soluble material remaining in the serum.

**DETAILS.** By means of a weighing pipet, weigh 5 grams of the latex into a 400-cc. beaker and immediately add about 200 cc. of distilled water. Cover with a watch glass and boil on a hot plate until the volume has been reduced by one half. Transfer to a 200-cc. volumetric phosphoric acid flask (this type of flask has a wide neck and is easily cleaned) and make up to within about 200 cc. of the mark. Add 1 cc. of 0.1 per cent methyl orange indicator solution and add 1 N sulfuric acid from a buret until

the red orange color, indicating a pH of about 4.3, is obtained and the rubber is well coagulated. Too much acid must not be added, as the sample will not coagulate well at an extremely low pH. Shake well to complete coagulation and make up to the mark. Filter the solution and pipet 100 cc. of the clear serum into a weighed evaporating dish. Evaporate to dryness on a steam bath and dry the residue in an air oven at 70° C. to constant weight.

The calculations are made as follows:

$$\text{Weight of solids} = \frac{\text{weight of sample} \times \% \text{ solids}}{100}$$
$$\text{Weight of water-solubles} = \frac{\text{weight of soluble matter in 100 cc. of diluted serum} \times (200 - \text{weight of solids})}{100}$$

From the weight of the total solubles subtract 0.0049 gram for every cubic centimeter of acid used and 0.001 gram for the weight of indicator. Then

$$\% \text{ water-solubles} = \frac{\text{corrected solubles weight}}{\text{weight of solids}} \times 100$$

The water-soluble matter in latex may be calculated roughly as the difference between the values obtained in the total solids and dry rubber content determinations. When an accurate value for the water-soluble material is not required, it may be calculated by means of this difference. However, in cases where it is important to know the water-soluble material accurately, it will be necessary to resort to the foregoing special procedure.

Determining Acetone Extract, L-12

**OUTLINE.** A dried-down latex film is extracted for 24 hours with pure acetone. The extract is dried to constant weight and the result expressed as percentage of extract based on the weight of dried film.

**DETAILS.** Sheet the dried film out as thin as possible on a cold mill (the temperature here should not exceed 40° C.), and use a 2-gram sample for extraction. Extract with freshly distilled acetone for 24 hours in an Underwriter's extraction apparatus. This extraction time will be sufficient for samples 0.0625 cm. (0.025 inch) or less in thickness. Evaporate the extract on a water or steam bath and dry to constant weight at 70° C. It is convenient to use for this purpose a flask which has been previously dried to constant weight at the same temperature. The result may be calculated as follows:

$$\text{Acetone extract in per cent} = \frac{\text{weight of extract}}{\text{weight of film sample used}} \times 100$$

*Precaution.* It is important to evaporate the acetone as specified over a water bath or a steam bath rather than over a hot plate, since overheating may occur and damage the extract even before all the acetone is removed.

Note on Mechanical Stability of Latex

The committee has omitted a procedure on mechanical stability of latex, since it was considered that the present tests had not been sufficiently developed and that their accuracy was not satisfactory. Work is in progress in the research laboratories of various companies for the purpose of developing a satisfactory test. It is hoped by the committee that suggestions for a satisfactory mechanical stability test will be received from abroad or the United States.

The same remarks apply to chemical stability.

Literature Cited

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# Reduction by Amalgamated Zinc

## Significant Factors in Efficiency

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The rate of reaction between an oxidant and zinc amalgam depends principally on the nature of the oxidant and the concentration of the zinc on the surface of the amalgam. In some cases, reduction is aided by removal of mercury by the oxidant, and in others, the formation of a liquid surface-amalgam takes place.

A large gradation of reduction rates was observed among the compounds examined.

THE amalgamation of zinc which is to be used for reduction in acid solution is a well-known practice. Although its effectiveness in decreasing the rate of reaction between zinc and hydrogen ion is well known, the possibility of a similar decrease in the activity of zinc towards other oxidants appears to have received little, if any, consideration. Recently, an observation of a decrease of zinc amalgam activity in the reduction of chrome alum solutions was reported by Stone and Beeson (12), who observed that the reduction by freshly prepared zinc amalgam proceeded rapidly at first, but decreased considerably after some use. It has since been found that by the time 2 per cent of the zinc has been consumed, the reaction becomes too slow to be of any practical value.

An investigation of the causes of this loss of activity has been made by the authors. The results have led to an understanding of the relative importance of various factors in reduction by amalgams, and of the mechanism by which such reduction takes place.

### Experimental Methods

In order to compare the relative effects of the various factors on the rate of reduction, a modified Jones reductor was used (Figure 1). The solution to be reduced was placed in the graduated reservoir and slowly forced upward through the amalgam by air pressure. In this upflow type of reductor, advantage is taken of the tendency of the liberated hydrogen to go with the flow of the liquid rather than against it as in the conventional form of the apparatus. Samples of the reduced solutions were measured with the 1-ml. microburet, and the concentrations determined by titration with suitable reagents. To exclude air, the top of the buret was sealed to a bulb filled with inert gas, as recommended by Crowell and Baumbach (3). Most of the reduced solution passed up into the bubble trap and out of the capillary regulator, which was inserted to ensure a steady rate of flow. After a run, the volume of hydrogen liberated was measured in an ordinary gas buret.

A standard weight of 20.0 grams of amalgam was used in a reductor of 8-mm. diameter. The solutions to be reduced were prepared 0.2 *N* in both the oxidant and hydrogen ion, unless it is specifically stated otherwise, and were passed through the reductor at rates ranging from 8 to 16 ml. per minute. If the rates of flow through different reductors are compared by calculating the milliliters of solution in contact with unit volume of 20-mesh zinc amalgam, per minute, a rate of 10 ml. per minute in the experimental reductor corresponds to a rate of 225 ml. per minute through a reductor of ordinary size containing about 250 grams of zinc. These comparatively high rates of flow were used to permit effects to be observed more readily. The results were plotted with the percentage reduction as ordinates and the total volume of oxidant passed through the reductor as abscissas.

The following factors were considered of sufficient importance to warrant detailed study: (1) the nature of the oxidant, as determined by the oxidation-reduction potential, the degree of ionization, stability of complexes, tendency to hydrolyze, and similar properties; (2) the degree of amalgamation; (3) the condition of the amalgam due to age, previous use, method of preparation, and manner of storage.

Other factors which were considered but not studied in detail include the temperature, the concentration of the solutions, the acidity, the size of the amalgam particles, and the effect of other ions in the solutions on the oxidation-reduction potentials of the reactants.

### Nature of the Oxidant

The position of an oxidant with respect to the mercury-mercurous couple in the oxidation-reduction potential series is a fundamental factor governing its behavior towards zinc amalgams. The stronger oxidants, such as ferric and ceric

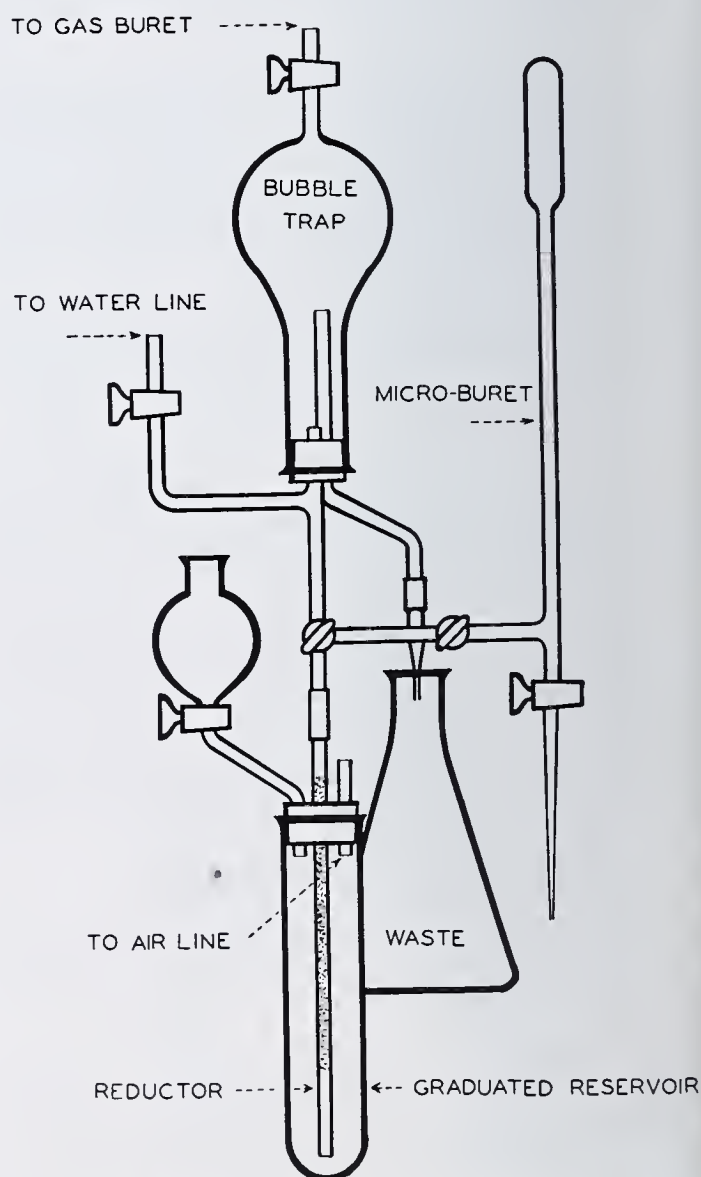


FIGURE 1. DIAGRAM OF APPARATUS



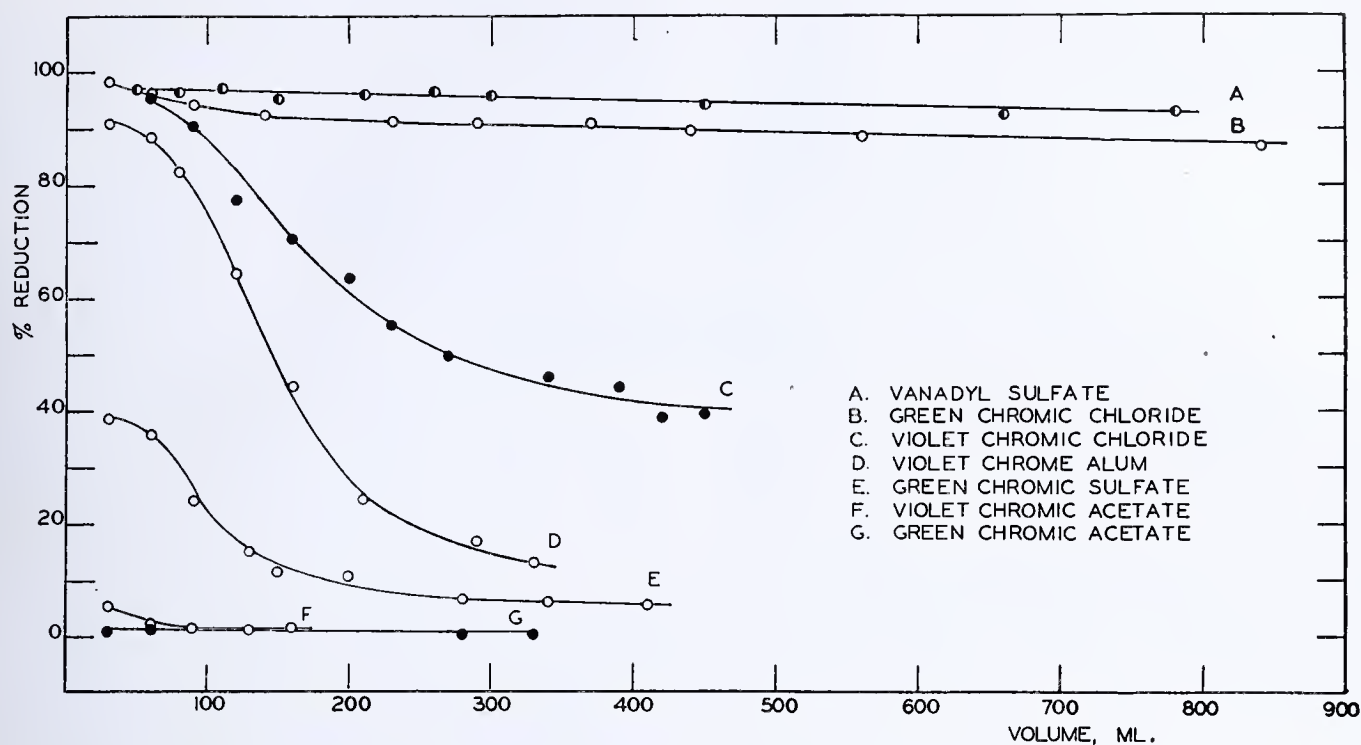


FIGURE 2. COMPARATIVE REACTION RATES OF VARIOUS COMPOUNDS WITH ZINC AMALGAMS CONTAINING 0.01 PER CENT MERCURY

Vanadium reduced,  $\text{VO}^{++}$  to  $\text{V}^{++}$ ; chromium,  $\text{Cr}^{+++}$  to  $\text{Cr}^{++}$ ; titanium,  $\text{Ti}^{++++}$  to  $\text{Ti}^{+++}$

ions, may be reduced by either the zinc or the mercury, while the weaker oxidants, such as chromic and titanous ions, must rely on the zinc alone for reduction. The presence of other ions in the solutions containing the oxidants may be significant. Ferric iron in hydrochloric acid solutions is quantitatively reduced by mercury, but in sulfuric acid the reaction reaches equilibrium at about 50 per cent reduction to ferrous (7).

The stronger oxidants which were investigated included ferric and ceric sulfates and potassium permanganate. With the standard 20-gram sample of amalgam (1 per cent mercury) and a rate of 10 ml. per minute, the reduction of 0.2 *N* solutions of these oxidants was quantitative and the amalgams showed no deterioration, even with considerable use. In one instance where ferric sulfate was being reduced, the reduction was continued until more than 35 per cent of the zinc had been used without any apparent drop in efficiency.

The behavior of the oxidants not reduced by free mercury is shown in Figures 2 and 3. The compounds reduced were commercial products save the hexaquo chromic chloride and the chromic acetates. The chloride was prepared according to the methods of Werner and Gubser (14) and Higley (6). The two chromic acetate complexes, which are of doubtful constitution, were the second violet and second green forms of Recoura (10), and were prepared according to his directions.

The prominent feature of this group of compounds is the more or less pronounced lowering of the rate of reaction after the amalgam has been in use for some time. The individual differences among the various chromic complexes, for example, were sufficiently characteristic to make the method usable as a qualitative test for identification of the pure salts.

Although contact of the reduced solutions with air was avoided in all cases, the oxygen dissolved in the reagent solutions was not usually removed. In the reduction of chromic salts, this resulted in values which were slightly low because of the rapidity of the reaction between chromous ion and oxygen. By complete removal of the dissolved oxy-

gen from the reagents, 100 per cent reduction was obtained with 0.2 *M* green chromic chloride, even at high rates of flow.

This result is of especial interest in view of the contradictory findings of previous investigators. Traube and Goodson (13) made the general statement that violet chromium complexes are more rapidly reduced than green, without having compared the chlorides. Demassieux and Heyrovsky (4) in polarographic measurements found that the green chloride is more easily reduced than the violet. Branham (2), on the contrary, reported the reduction of green chromic chloride by zinc amalgam to be very slow and to require a large excess of hydrochloric acid. In the present investigation it was found that freshly prepared solutions of green chromic chloride made from the dry salt were rapidly and completely reduced by amalgamated zinc, with or without the addition of acid. The material used was the J. T. Baker Chemical Company c. p. product, which was found on analysis (by precipitation of ionizable chloride with silver nitrate in the cold) to be the dichlorotetraquo complex described in the literature. It was also found that a solution of chromous chloride which had been oxidized by air to chromic (thus forming hydroxo and other basic complexes, 1) gave a very low reduction rate. Since it is known that chromic chloride standing in the presence of water forms such basic complexes (11), many of which are stable to acid, the lack of agreement between different workers may be due to the use of such material.

A plausible explanation for the difference in reduction rates of the violet (hexaquo) chromic chloride and sulfate (chrome alum) lies in the tendency of both the violet chloride and sulfate in solution to form equilibrium mixtures with the green modifications (5, 9). Since the green sulfate reduces very slowly and the green chloride very rapidly, the differences observed are understandable.

When amalgams containing 0.01 per cent of mercury were used, the rate of hydrogen evolution from 0.2 *N* hydrochloric acid was found to fall off in the same manner as the rate of reduction of the green chromic sulfate. The rate of reduction is lessened greatly by the presence of other oxidizing agents,



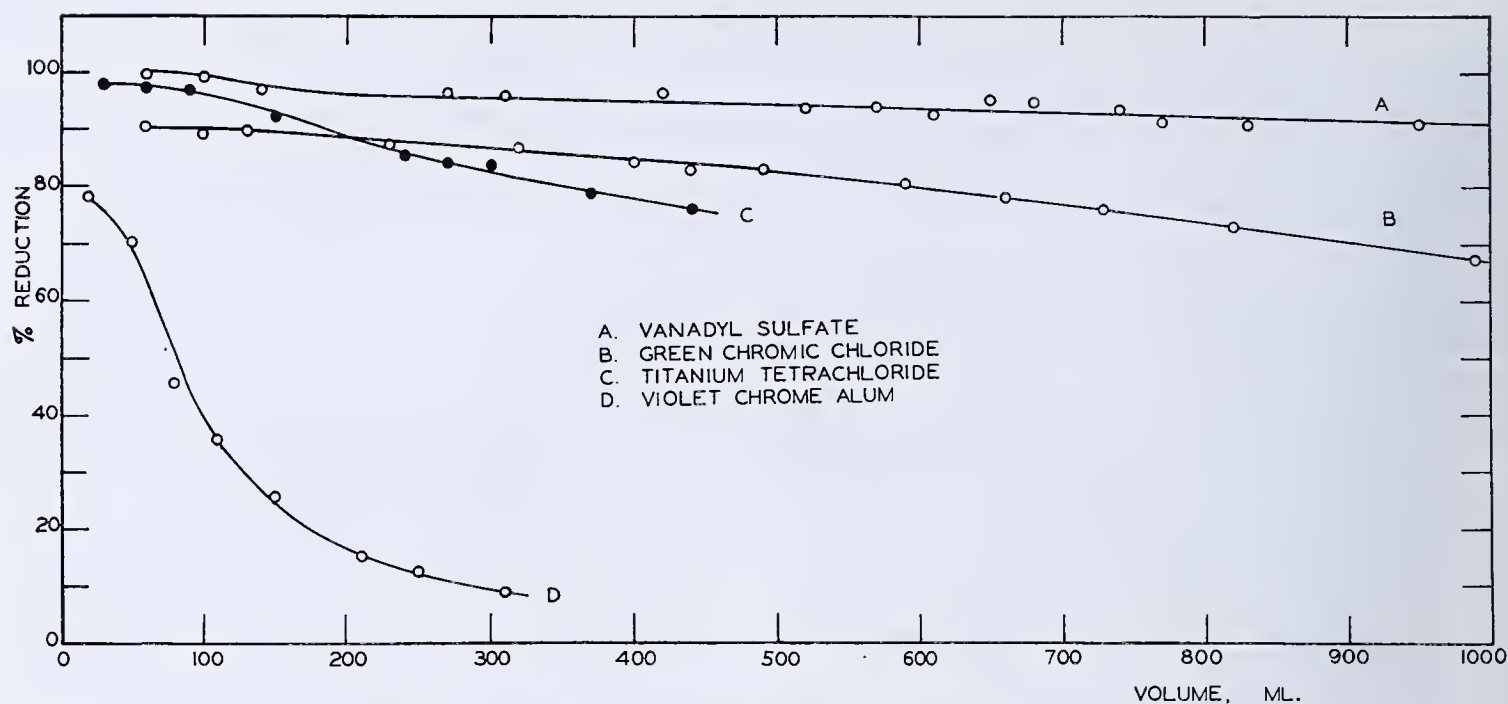


FIGURE 3. COMPARATIVE REACTION RATES OF VARIOUS COMPOUNDS WITH ZINC AMALGAMS CONTAINING 1.0 PER CENT MERCURY

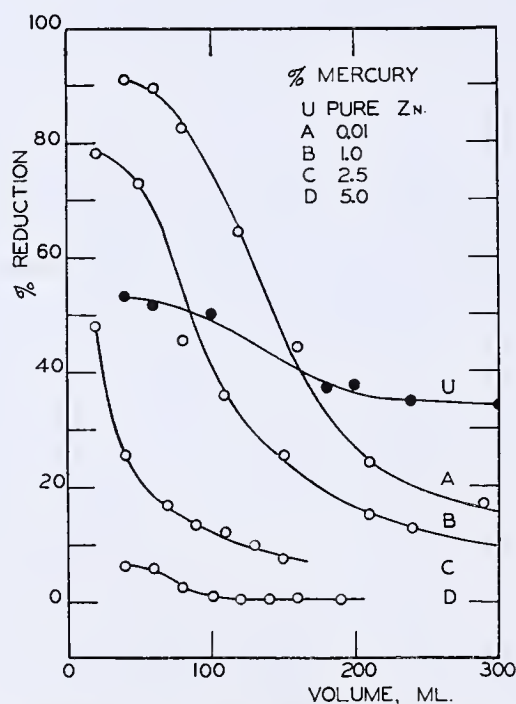


FIGURE 4. COMPARATIVE REACTION RATES OF CHROME ALUM SOLUTIONS With zinc amalgams containing various proportions of mercury

though only slightly by salt solutions alone. The volume of hydrogen given off in unit time from pure 0.2 *N* hydrochloric or sulfuric acid is approximately double that evolved from chromic chloride or chrome alum dissolved in the corresponding acid. The various oxidants have slightly different effects on the rate of the hydrogen ion-zinc reaction. In the course of long runs with the stronger oxidants, such as ferric iron, the rate of hydrogen evolution would increase markedly.

#### Degree of Amalgamation

The ideal amalgam should give rapid and complete reduction of the desired substance with minimum liberation of hydrogen. Published directions are often vague and frequently contradictory, the percentages of mercury recommended varying from 0.1 per cent to as much as 10 per cent. During the present investigation, amalgamation was ac-

complished by washing 20-mesh zinc for 1 minute in sufficient 1 *N* hydrochloric acid to cover it, adding the proper amount of 0.25 *M* mercuric nitrate or chloride, and stirring rapidly for 3 minutes. The solution was then decanted from the amalgam, which was washed and stored under water containing a few drops of hydrochloric acid. Analysis of the decanted liquid and washings showed that within 3 minutes the mercury was 95 to 100 per cent reduced in the preparation of amalgams containing as much as 10 per cent of mercury, indicating that the reaction is very rapid. The chloride and nitrate seem to be equally satisfactory.

The effect of varying the percentage of mercury in the amalgam on the rate of reduction of chrome alum and green chromic chloride is seen in Figures 4 and 5. The solutions were

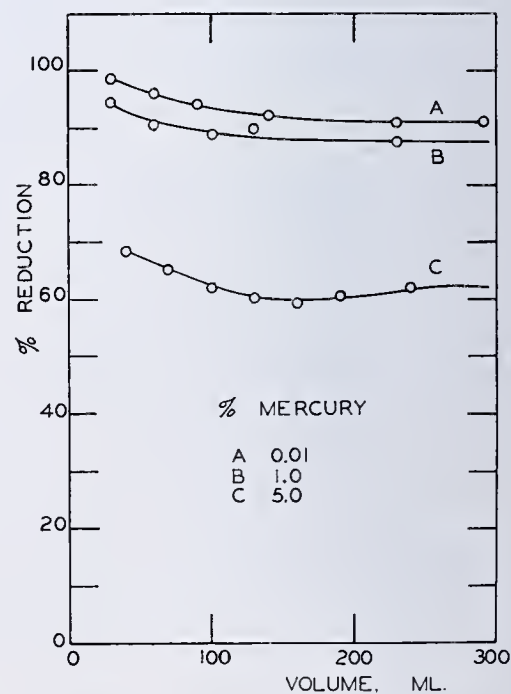


FIGURE 5. COMPARATIVE REACTION RATES OF GREEN CHROMIC CHLORIDE SOLUTIONS

With zinc amalgams containing various proportions of mercury. Flow of solution through reductor in run with 5 per cent amalgam was interrupted for 3 minutes at 170-ml. point



0.2 M in chromium and in acid. The low reduction rate with unamalgamated zinc is probably due to hydrogen gas, while the decline exhibited might be explained by the disappearance of broken crystal faces in the zinc.

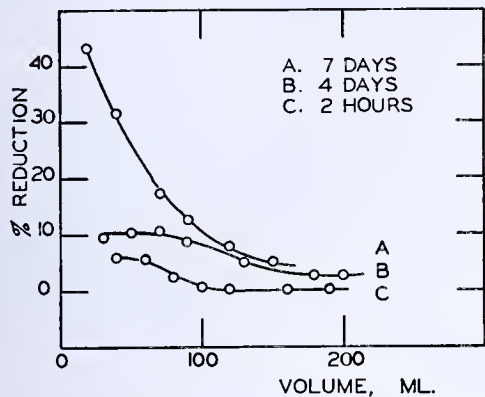


FIGURE 6. COMPARATIVE REACTION RATES OF CHROME ALUM  
With zinc amalgams containing 5 per cent mercury, allowed to stand for various lengths of time before use

The effect of time on heavily amalgamated but unused samples of zinc is shown in Figure 6. As the amalgams are allowed to stand in slightly acid water, they become more active. It was found, however, that lightly amalgamated samples, which were active when fresh, became coated with a white precipitate and lost much of their activity if allowed to become dry in air or even to stand in water exposed to the air for long periods of time.

Surface Effects during Reduction

From the evidence which has been presented, certain conclusions have been drawn. Under the conditions of the experiments, the governing factor in the rate of reduction of a given weak oxidant is the amount of available zinc at the surface of the amalgam, and the depletions which were observed were due to the lowering of the concentration of the zinc in the surface layers. Diffusion of zinc through solid amalgams is very slow, heating being necessary to obtain a rapid revival of activity. Light amalgams were completely restored by heating for an hour in an atmosphere of nitrogen at about 400°. The stronger oxidants were reduced by both the zinc and mercury rapidly enough so that depletion effects did not appear. That mercury is actually removed from portions of the amalgam surface is shown by the increased amounts of hydrogen which were obtained.

The absence of observable depletion effects during the reduction of green chromic chloride and vanadyl sulfate is due to the formation of a liquid amalgam surface, through which the diffusion of fresh zinc is sufficiently rapid to keep pace with the removal by oxidation. This view is supported by a number of facts. During runs with titanous chloride and chrome alum, for example, the particle size was found to remain uniform throughout the reductor. However, with green chromic chloride and vanadyl sulfate, the particles at the entrance of the reductor became greatly reduced in size without any visible change in the others. In one instance, approximately one third of the zinc was dissolved under these conditions.

For a short time after amalgamation, especially with larger amounts of mercury, a definite surface liquidity could be observed. On standing in contact with one another, the particles would set into a single mass which could be crumbled into permanently discrete particles. The same behavior was observed in amalgams which had been used in the reduction of considerable amounts of green chromic chloride. The forma-

tion of visible amounts of liquid amalgam could also be observed in the reduction of hydrogen ion when the amalgam was vigorously shaken to avoid polarization.

In a typical experiment, in which 20 grams of amalgam (0.01 per cent mercury) were placed in a bottle with a large excess of 6 N sulfuric acid and mechanically shaken, a variation of rate of hydrogen evolution with time was obtained which is shown in Figure 7. Under these conditions, the grinding effect due to shaking assists in bringing fresh zinc to the surface, so that a steady state is not reached at the minimum rate.

The reaction rates of chrome alum and green chromic chloride with liquid zinc amalgams were determined by the methods of Masuda (8) and it was found that the chloride is reduced definitely more rapidly than the alum. Unfortunately, the method does not give conditions analogous to those in the ordinary reductor.

When a reductor is used, there is always plenty of fresh zinc available just below the surface layer if the amalgamation is light, allowing rapid replenishment whenever the outer layer becomes liquid. With a heavy coating of mercury on the surface, fresh zinc must come from and through layers of amalgam and not pure zinc. Similar conditions affect the activity of freshly prepared amalgams. Here, also, the heat of reaction from the reduction of mercuric ion makes possible a more rapid diffusion of zinc to the surface.

Recommendations for Practical Amalgamation

The amount of mercury which it is desirable to deposit on the zinc in practical work is dependent principally on the acidity of the solution, the type of oxidant, the size of the reductor, and the rate at which the solution is to be passed through the reductor.

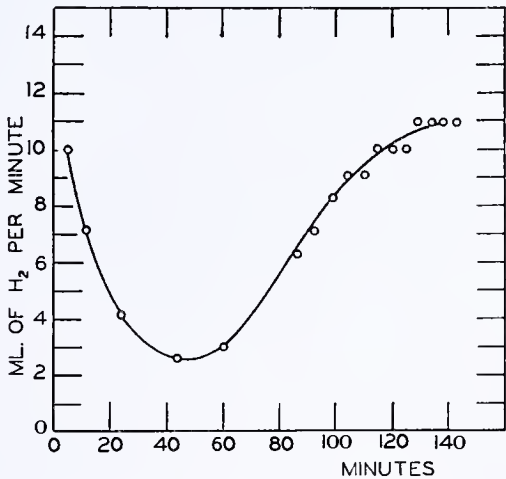


FIGURE 7. RATE OF EVOLUTION OF HYDROGEN FROM 6 N SULFURIC ACID  
By action of zinc amalgam (0.01 per cent mercury), under vigorous agitation

In working with oxidants which are not reduced by mercury, the least amount of mercury which will enable satisfactory control of hydrogen evolution should be used, since heavy amalgamation tends to reduce the rate of reaction. With acid concentrations of about 0.2 N or less, 0.1 per cent of mercury is satisfactory for oxidants such as chrome alum or vanadyl sulfate, but the use of more than 1 per cent of mercury is likely to result in too slow a reduction rate. For those oxidants which are reduced by mercury as well as by zinc, and particularly at higher acid concentrations, as much as 5 per cent of mercury may be desirable.

The results of this work indicate that with a 2 × 30 cm. reductor charged with 20-mesh amalgamated zinc, the cus-



tomary rates of flow are in many cases unnecessarily slow. For those oxidants tried which reacted with free mercury, a rate of 200 ml. per minute was not too rapid for complete reduction. The oxidants not reduced by mercury usually require a somewhat lower rate of flow through the reductor, especially after the amalgam has had considerable use. For any given oxidant not studied in this work, it would not be possible to predict the limiting conditions for percentage of mercury and rate of flow. However, a comparison with the types given should indicate something of what might be expected.

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# Determination of Furfural in Furfural-Furfuryl Alcohol Solution

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IN THIS laboratory it has been necessary to make a large number of analyses for furfural in solution in furfuryl alcohol. It was desirable to have a simple, rapid method with a reasonable degree of accuracy.

A study of the analytical procedures for the determination of this aldehyde revealed that the phloroglucinol (1), thio-barbituric acid (7), and 2,4-dinitrophenylhydrazine (10) methods, which are gravimetric, are much too slow. The Hughes-Acree (5) and Kullgren-Tyden (8) methods, which are volumetric, involve the addition of bromine to the furan ring and are therefore inapplicable for the analyses under consideration. The hydroxylamine hydrochloride method (2), which is comparatively rapid, is complicated by a difficultly reproducible end point.

These difficulties have been substantially eliminated by a method based on the reaction of furfural with sodium bisulfite. This reaction was first applied to aldehyde determinations by Ripper (11) and Feinberg (3) and was later adapted to furfural by Jolles (6), but the method as applied by these workers has been shown to be highly inaccurate in most cases (9). The sources of inaccuracy are variations in temperature, hydrogen-ion concentration, the concentration of aldehyde in the solution to be analyzed, the excess of bisulfite used, the dissociation constant of the addition products formed, and the time allowed for the reaction. In the present method some of these conditions are constant and the use of the proper correction factor compensates for the effect of the others.

### Reagents

Approximately 0.1 *N* sodium bisulfite solution is prepared by dissolving 5.2 grams of acid sodium sulfite ( $\text{NaHSO}_3$ ) in distilled water and diluting to 1 liter. The effective concentration of this solution is redetermined for each series of analyses by titrating with 0.1 *N* iodine.

The iodine solution is prepared by dissolving 12.6 grams of resublimed iodine and 25 grams of potassium iodide in distilled water and diluting to 1 liter. This iodine solution is restandardized frequently against 0.1 *N* sodium thiosulfate, using starch solution as an indicator.

### Preparation of Samples

From a determination of the density or the refractive index or by a rough analysis an estimate is made of the concentration of furfural in the solution to be analyzed.

If the solution contains 0 to 9 per cent of furfural, approximately 10 grams are weighed out and made up to 100 ml. with distilled water in a volumetric flask. If the estimate shows 10 to 100 per cent of furfural a quantity is weighed out such that, when

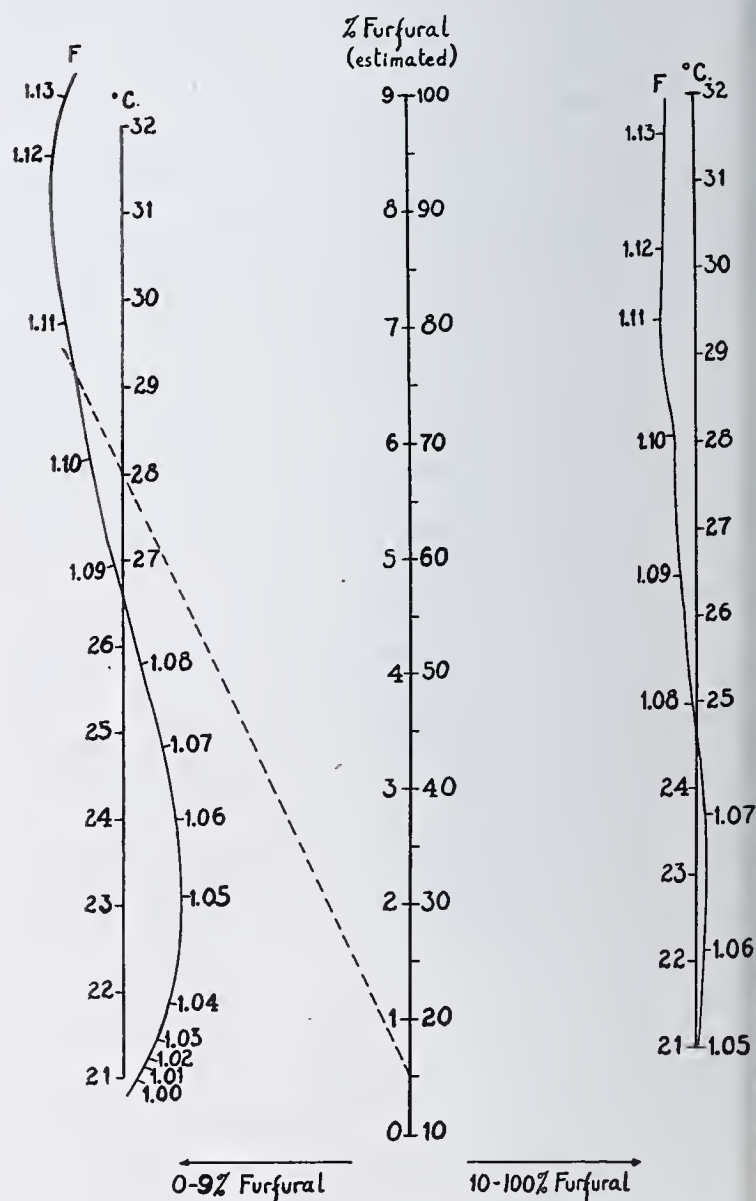


FIGURE 1. NOMOGRAPHS



diluted to 100 ml. with distilled water, the resulting solution contains approximately 1 gram of furfural. If the solution for analysis is difficultly soluble in water, ethyl alcohol may be substituted as the solvent. Tests in this laboratory have shown that this substitution has no effect on the amount of iodine required for titration. From this point on, the procedure is exactly the same, regardless of the concentration of furfural in the original solution.

Analysis

Five milliliters of the prepared furfural solution are transferred to a glass-stoppered Erlenmeyer flask (100 to 150 cc.) and 25 ml. of the sodium bisulfite solution are added. The resulting mixture is shaken and allowed to stand for 15 minutes (±1 minute). In the intervening time, 25 ml. of the same sodium bisulfite solution are added to a similar Erlenmeyer flask, and allowed to stand for 15 minutes (±1 minute). Then 3 to 4 drops of starch solution are added to each of the samples which are then titrated with 0.1 N iodine solution. The time for the titrations should be kept within 1 to 2 minutes.

Having completed this step, the concentration of furfural in the sample being analyzed is obtained by use of the following equation, where *F* is a correction factor which is determined from the nomographs (Figure 1).

Per cent of furfural = 
$$\frac{F(\text{ml. of } 0.1\text{ N I}_2 \text{ control} - \text{ml. of } 0.1\text{ N I}_2 \text{ sample}) \times 0.0048 \times 20 \times 100}{\text{weight of sample}}$$

Explanation of Nomographs

The center line of the graph serves a twofold purpose, the left side indicating concentrations of furfural from 0 to 9 per cent and the right indicating concentrations from 10 to 100 per cent. The nomograph on the left side of the page refers to the left side of the concentration line, whereas that on the right refers to the right side of the concentration line. Having estimated the concentration of furfural in the sample to be analyzed, the correction factor, *F*, is determined by laying a straight-edge across the appropriate nomograph from the estimated point on the concentration line to the point representing the room temperature. The intersection of the straight-edge and the factor curve of the nomograph gives *F* to the nearest hundredth.

Data

The furfural and furfuryl alcohol used were prepared from the technical grade of each by fractionating three times under vacuum, discarding approximately 15 per cent of the total volume at the beginning and end of each distillation.

Solutions of these products of known concentration were analyzed by three different laboratories, using the procedure described above.

Sample Calculation

Solution 2 (Table I) was estimated to contain 0.5 per cent of furfural; hence a sample of approximately 10 grams (10.5096 grams) was weighed out and made up to 100-ml. volume with distilled water. The analysis was performed in triplicate at a temperature of 28° C., and the amount of iodine solution required was 21.76, 21.77, and 21.75 ml., respectively. The control solution required 22.69 ml. to the same end point, which is a difference of 0.93 ml. of 0.1025 N iodine. *F* was determined by placing a straight-edge on the left-hand nomograph from 0.5 per cent furfural to 28° C., whence *F* was found to be 1.11. The concentration of furfural in the sample was then calculated by substituting these values in the equation shown above.

Per cent of furfural = 
$$\frac{1.11 \times 0.93 \times 0.0048 \times 1.025 \times 20 \times 100}{10.5096} = 0.97$$

Comparison with Other Methods

Table II shows the results obtained in analyzing furfural by the thiobarbituric acid, hydroxylamine hydrochloride, and 2,4-dinitrophenylhydrazine methods (4), compared with re-

TABLE I. ANALYSES OF FURFURAL IN SOLUTION IN FURFURYL ALCOHOL

Solution No.	Furfural Present %	Furfural Found			
		Lab. 1 %	Lab. 2 %	Lab. 3 %	Average %
1	0.00	0.00	0.20	0.10	0.10
2	0.96	0.97	1.32	1.21	1.17
3	1.61	1.61	1.72	1.70	1.68
4	2.11	2.14	2.10	2.18	2.14
5	4.36	4.66	4.66	4.67	4.66
6	5.49	5.44	5.82	5.37	5.54
7	8.78	8.66	8.85	8.68	8.73
8	14.99	15.02	15.44	...	15.23
9	32.98	33.41	33.07	33.40	33.29
10	45.50	45.19	...	...	...
11	62.70	62.61	63.62	62.68	62.97
12	100.00	100.20	101.26	100.80	100.75

TABLE II. FURFURAL FOUND ON ANALYZING FURFURAL

Sample No.	Thio-barbituric Acid (?) %	Hydroxyl-amine Hydro-chloride (2) %	2,4-Dinitro-phenyl-hydrazine (10) %	Bisulfite-Iodine %
1	103.92	100.52	99.33	100.20
2	102.49	101.63	98.83	101.26
3	103.39	102.35	97.81	100.80
4	104.35	...	98.88	...
5	103.14	...	...	...
6	102.85	...	...	...
7	104.13	...	...	...
Av.	103.47	101.50	98.71	100.75

sults obtained by the present method. It indicates the comparative accuracy of the methods when analyzing pure furfural.

Discussion

Rapid and reasonably accurate analyses for furfural in solution in furfuryl alcohol may be made by the bisulfite-iodine method when applied as described in this article. When analyzing solutions of high furfural concentration, the accuracy is within 1 per cent of the true value. Larger deviations are found when working with solutions of low furfural content.

The authors' experience has shown that solutions of furfural in furfuryl alcohol on standing undergo some change which affects their solubility in water and produces high results when they are analyzed by the present method. This factor has not been investigated, inasmuch as the solutions for analyses in this laboratory were never more than 2 days old.

Acknowledgment

Acknowledgment is hereby made of the initial development work on this method by J. Pokorny, G. S. Blakeslee and Company, Chicago, Ill.

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# Composition of Lithium and Potassium Salts Precipitated by Uranyl Acetate Reagents for Sodium

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**T**HOUGH various investigators have shown that certain uranyl acetate reagents for sodium precipitate lithium also when added to lithium solutions of moderate concentration, considerable uncertainty seems to exist as to the composition of the precipitates so produced. Certain investigators believe that the lithium precipitates are only double acetates of lithium and uranyl, whereas others have concluded that they are triple acetates analogous in composition to those produced by the interaction of these reagents with sodium solutions.

Chamot and Bedient (4) state that they were unable to prepare a triple acetate in which lithium replaced sodium, and conclude in general that, of the members of Group I of the periodic system, sodium alone yields a triple uranyl acetate containing magnesium, zinc, cadmium, cobalt, nickel, iron, manganese, or copper. On the other hand, Insley and Glaze (6), and later Miller and Travers (9), have shown rather conclusively by careful analyses that the precipitate produced by the addition of the zinc uranyl acetate sodium reagent to lithium solutions is a triple acetate analogous in composition to the hexahydrated sodium zinc uranyl acetate produced by the addition of this same reagent to sodium solutions. Moreover, Feldstein and Ward (5) found that the precipitate formed by the addition of their nickel uranyl acetate reagent to lithium solutions contained lithium, nickel, and uranium, though apparently no quantitative analysis of this salt was made. No careful analysis appears to have been made of the lithium salt precipitated by any of these sodium reagents other than zinc uranyl acetate.

The information available in the literature concerning the composition of the precipitates produced in potassium solutions of sufficiently high concentration by the uranyl acetate reagents for sodium is likewise incomplete and contradictory. Thus, for example, Kolthoff in one paper (8) speaks of the potassium precipitate formed by the zinc type of reagent as potassium uranyl acetate, whereas in another paper (7) he calls it the triple salt, potassium zinc uranyl acetate. Barber and Kolthoff (1) describe it as potassium zinc uranyl acetate, and Insley and Glaze (6) in their study of the crystal form and structure of the salt precipitated from potassium solutions by the zinc uranyl acetate reagent likewise consider it to be this triple salt. On the other hand, Feldstein and Ward (5) state that the precipitate produced by the addition of nickel uranyl acetate reagent to potassium solutions is not a triple salt but only the double salt, potassium uranyl acetate.

No quantitative analysis appears to be given anywhere of the precipitate produced in potassium solutions by any type of uranyl acetate sodium reagent. Various views concerning the composition of these precipitates have been repeated by later workers or have been extended by analogy to the composition of precipitates produced by types of reagents other than the two specifically mentioned. Unfortunately this has further increased the confusion concerning the nature of these precipitates. In view of the incomplete and conflicting information concerning the composition of these lithium and potassium precipitates it seemed worth while to investigate their composition critically. This involved the preparation of all the possible general types of uranyl acetate reagents for sodium, including some not previously described, the precipitation of lithium and potassium in various ways by these reagents, and the careful analysis of the precipitates thus obtained. Since any one reagent of a given type, such as magnesium uranyl acetate, for example, was found to yield precipitates of the same composition in spite of minor variations

in the formula of the reagent, the only experiments here described are those that were made with a series of reagents prepared according to a similar general formula—the one that is usually followed in the preparation of those uranyl acetate sodium reagents that have come into general use.

## Preparation of Reagents

The magnesium uranyl acetate reagent was prepared according to the directions of Caley and Sickman (3). The zinc uranyl acetate reagent was prepared in a similar way, except that 200 grams of zinc acetate dihydrate were used in place of the specified quantity of magnesium acetate tetrahydrate. The nickel uranyl acetate reagent was prepared according to the directions given by Feldstein and Ward (5). The cobalt, manganese, and cadmium uranyl acetate reagents were prepared like the nickel uranyl acetate reagent except that 200 grams each of cobalt acetate tetrahydrate, manganese acetate tetrahydrate, and cadmium acetate dihydrate, respectively, were used.

Though the ferrous uranyl acetate reagent was prepared according to the same basic formula, the ease with which concentrated ferrous acetate solution oxidizes on contact with air necessitated a special method of preparation. The solution of ferrous acetate was made by dissolving equivalent quantities of barium acetate monohydrate and ferrous sulfate heptahydrate in separate portions of water freed from dissolved oxygen, mixing these two solutions, filtering off the precipitated barium sulfate, and concentrating the resulting solution under reduced pressure. The concentrated ferrous acetate solution was then mixed with a previously prepared solution containing the uranyl acetate and acetic acid. This whole process was carried out with nitrogen gas above the solutions.

In the preparation of the mercuric and copper uranyl acetate reagents, the same quantities of uranyl acetate, acetic acid, and water were used as for the nickel uranyl acetate reagent, but the weights of the divalent acetates taken were of necessity less than 200 grams because of the lower solubilities of these acetates. For the mercuric uranyl acetate reagent 100 grams of the anhydrous salt were used and for the copper uranyl acetate reagent 70 grams of cupric acetate monohydrate. After mixing, all these reagents were maintained at 20° C. for at least an hour before they were filtered into dry containers.

## General Experimental Procedure

All precipitations of lithium were made from concentrated lithium acetate solutions prepared by dissolving pure lithium carbonate in concentrated acetic acid. The lithium carbonate was purified, especially for the purpose of eliminating sodium, by the method of recrystallization devised by Caley and Elving (2). The volume of reagent used for all precipitations was 100 ml. During precipitation the solutions were stirred mechanically for 1 hour at 20° C., after which the lithium precipitates were filtered off on weighed glass filter crucibles, washed with eight 5-ml. portions of 95 per cent ethyl alcohol, and dried to constant weight, usually at 100° to 105° C. All precipitations of potassium were made from concentrated potassium chloride solutions under the same conditions as to volume of reagent, time allowed for precipitation, and method of filtration and washing. The potassium precipitates were usually dried to constant weight at room temperature. The samples for analysis were then taken from the dried lithium and potassium precipitates.

## Composition of Lithium Precipitates

Regardless of rather wide experimental variations in the volume and concentration of the lithium solutions, the salts precipitated from these solutions by all the reagents that formed precipitates were always found to be triple acetates



analogous in composition to the triple acetates precipitated from sodium solutions by these same reagents.

**LITHIUM MAGNESIUM URANYL ACETATE.** In the first preparation 1.100 grams of lithium carbonate were dissolved in 6 ml. of glacial acetic acid and 4 ml. of water and precipitated with the standard volume of magnesium uranyl acetate reagent. The yield was 3.39 grams. In the second preparation 0.551 gram of lithium carbonate was dissolved in 4.5 ml. of glacial acetic acid and likewise precipitated. The yield was 3.42 grams.

In the analysis of these preparations the uranium was precipitated as ammonium diuranate with carbonate-free ammonium hydroxide and weighed as  $U_3O_8$ . The same method for the determination of the uranium was used in the analysis of all the other precipitates. The magnesium was precipitated in the filtrate from the uranium separation with 8-hydroxyquinoline and weighed as the hydroxyquinolate. In the analysis of the first preparation the lithium was weighed as sulfate after evaporation of the magnesium filtrate. In the analysis of the second preparation the lithium in one sample was determined as sulfate, and in the other as phosphate. By reason of the excessive time required for the determination of lithium as sulfate or phosphate, in the analysis of the other precipitates the lithium was precipitated as the aluminate and weighed in this form after the separation of the uranium and the divalent metal.

The following results were obtained in the analysis of these two preparations:

	Uranium %	Magnesium %	Lithium %
Found:			
Preparation 1	48.17	1.58	0.49
Preparation 2, sample a	48.12	1.63	0.52
Preparation 2, sample b	48.15	1.64	0.44
Calculated:			
$LiMg(UO_2)_2(C_2H_3O_2)_9 \cdot 6H_2O$	48.23	1.64	0.47

It is obvious that analysis of the lithium salt precipitated by the magnesium uranyl acetate reagent gives results that correspond closely to the theoretical figures for the hexahydrated triple salt.

**LITHIUM COBALT URANYL ACETATE.** A lithium acetate solution prepared by dissolving 0.506 gram of lithium carbonate in 6 ml. of glacial acetic acid gave 3.63 grams of triple salt on precipitation with the cobalt uranyl acetate reagent.

For analysis the uranium was separated by a double precipitation, and in the filtrate the cobalt was precipitated with  $\alpha$ -nitroso- $\beta$ -naphthol and weighed as  $Co_3O_4$ . After removal of the excess of the organic reagent from the cobalt filtrate the lithium was determined as  $LiH(AlO_2)_2 \cdot 5H_2O$  by a modification of the method suggested by Prociv (10).

The following results were obtained on the analysis of this preparation:

	Uranium %	Cobalt %	Lithium %
Found	46.73	3.67	0.51
Calculated:			
$LiCo(UO_2)_2(C_2H_3O_2)_9 \cdot 6H_2O$	47.13	3.89	0.46
$LiCo(UO_2)_2(C_2H_3O_2)_9 \cdot 7H_2O$	46.57	3.84	0.45

Here the agreement of the analysis with the theoretical figures for the hexahydrated triple salt is less satisfactory than for the lithium magnesium uranyl acetate. Indeed, the analytical results correspond better with the theoretical figures for a heptahydrated lithium cobalt uranyl acetate. However, the lack of agreement with the theoretical figures for the hexahydrate is no certain indication that the cobalt salt is a higher hydrate since the discrepancy may be explained in other ways, such as the presence of some hygroscopic water in the sample taken for analysis. The essential fact is clear enough—namely, that the salt precipitated from lithium solutions by cobalt uranyl acetate reagent is a triple salt.

**LITHIUM NICKEL URANYL ACETATE.** A lithium acetate solution prepared by dissolving 0.499 gram of lithium carbonate in 6 ml. of glacial acetic acid gave 4.35 grams of triple salt on precipitation with the nickel uranyl acetate reagent. The yield in this precipitation is markedly higher than in the precipitations made with the other reagents under analogous conditions. This higher yield is probably an indication that the lithium nickel uranyl acetate is less soluble than any other of these lithium triple salts. The

nickel salt is also distinguished from the other triple salts by its color, which is bright green, the colors of the other triple salts being various shades of yellow.

For analysis the uranium was separated by a double precipitation, and in the filtrate the nickel was determined with dimethylglyoxime. After removal of the excess of organic reagent from the nickel filtrate the lithium was determined.

The following results were obtained on analysis:

	Uranium %	Nickel %	Lithium %
Found:			
Sample a	46.13	3.91	0.45
Sample b	46.40	3.87	0.57
Calculated:			
$LiNi(UO_2)_2(C_2H_3O_2)_9 \cdot 6H_2O$	47.14	3.87	0.46
$LiNi(UO_2)_2(C_2H_3O_2)_9 \cdot 7H_2O$	46.58	3.83	0.45

The results for the uranium content of this nickel salt are even further from the theoretical figure for a hexahydrated triple salt and nearer the theoretical figure for a heptahydrated triple salt than the result obtained for the uranium content of lithium cobalt uranyl acetate. On the other hand, the results for the nickel content of the triple salt, very likely the most accurate of the three determinations, are definitely closer to the theoretical figure for the hexahydrate. This discrepancy, which is certainly real and not an apparent one arising from defects in the analytical method, cannot be ascribed to improper drying but probably to a slight decomposition of the salt by the method of washing required to separate the salt from the reagent. That a slight amount of selective leaching out of component salts of certain complex uranyl acetates may occur on washing with alcohol is demonstrated clearly by the examination of the salt precipitated from potassium solutions by these reagents. However, the above results show clearly enough that the salt precipitated from lithium solutions by the nickel uranyl acetate reagent is also a triple salt.

**LITHIUM IRON URANYL ACETATE.** A lithium acetate solution prepared by dissolving 0.450 gram of lithium carbonate in 7 ml. of glacial acetic acid gave 2.16 grams of triple salt on precipitation with the ferrous uranyl acetate reagent. To prevent oxidation of the reagent during precipitation an atmosphere of nitrogen was maintained above the reaction mixture. Because of the likelihood of change in composition by oxidation on oven-drying, the preparation was not dried at 100° to 105° C. as were all the other preparations of these triple salts, but was allowed to stand exposed to air at room temperature until the weight became constant. No change in the appearance of the crystals of the salt was observed after exposure to air for 24 hours.

For analysis the iron was separated first by precipitation with cupferron, the precipitate being ignited to ferric oxide for weighing. After removal of the excess of organic reagent the uranium and the lithium were separated and determined in the usual way.

The results of the analysis were as follows:

	Uranium %	Iron %	Lithium %
Found	45.53	3.38	0.35
Calculated:			
$LiFe(UO_2)_2(C_2H_3O_2)_9 \cdot 6H_2O$	47.22	3.69	0.46
$LiFe(UO_2)_2(C_2H_3O_2)_9 \cdot 9H_2O$	45.59	3.56	0.44

From this analysis it would appear that the air-dried preparation might be a hexahydrated triple salt containing a considerable proportion of hygroscopic moisture or that it might be a higher hydrate. The first possibility seems rather unlikely because the crystals taken for analysis appeared entirely dry. The second is more likely, especially in view of investigations that have been made on the composition of air-dried sodium triple acetates. Certain of these analogous salts have been found to exist as hydrates containing more than six molecules of water, the highest reported being nine molecules, which also appears to be the water content of this air-dried lithium iron uranyl acetate.

**LITHIUM MANGANESE URANYL ACETATE.** A lithium acetate solution prepared by dissolving 0.524 gram of lithium carbonate in 6 ml. of glacial acetic acid gave only a few minute crystals on



TABLE I. COMPARATIVE SENSITIVITY OF REAGENTS TOWARD SODIUM

Type of Reagent	10 mg.	5 mg.	2 mg.	1 mg.	0.5 mg.	0.2 mg.	0.1 mg.
Magnesium	+	+	+	+	+	+	+
Nickel	+	+	+	+	+	+	+
Cobalt	+	+	+	+	+	+	+
Zinc	+	+	+	+	+	+	+
Manganese	+	+	+	+	—	—	—
Copper	+	+	+	+	—	—	—
Cadmium	+	+	—	—	—	—	—
Mercury	—	—	—	—	—	—	—

precipitation with the manganese uranyl acetate reagent. In another preparation a lithium solution made by dissolving 1.016 grams of lithium carbonate in 10 ml. of glacial acetic acid gave only 0.341 gram of triple salt on precipitation with the reagent. Evidently the triple salt containing manganese is much more soluble than the other lithium triple salts here described.

For analysis the uranium was separated by a double precipitation, and in the filtrate the manganese was precipitated as the phosphate and weighed as the pyrophosphate. Because of the small size of the sample available for analysis no attempt was made to determine the lithium, though this element was qualitatively found to be a constituent of the salt.

The results of the analysis were as follows:

	Uranium %	Manganese %
Found	46.96	3.52
Calculated:		
$\text{LiMn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$	47.25	3.63
$\text{LiMn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 7\text{H}_2\text{O}$	46.69	3.59

The result for the manganese content is nearer to the theoretical figure for the heptahydrate than for the hexahydrate, and the result for the uranium content lies between the theoretical figures for the two hydrates. As with the other triple salts of this series, with the possible exception of the magnesium and zinc salts, there is also some uncertainty as to the degree of hydration of this salt, though there is no uncertainty that it is a triple acetate.

**NONPRECIPITATION OF LITHIUM BY CERTAIN REAGENTS.** In similar experiments with the cadmium, mercury, and copper uranyl acetate reagents no precipitates were formed on mixing these reagents with the concentrated lithium acetate solutions, nor did any precipitates form even after vigorous stirring for considerable periods. It seems doubtful, therefore, whether the corresponding lithium triple salts exist, or, at least, whether they can be separated out by this method.

The cadmium and mercury uranyl acetate reagents are so insensitive toward sodium ion that they are of little practical value as analytical reagents, but the copper uranyl acetate reagent is a fairly sensitive reagent for sodium. This difference is illustrated by the results in Table I which were obtained by mixing 5 ml. of a given reagent with 1 ml. of sodium chloride solution and observing the presence or absence of a precipitate at the end of 30 minutes.

Though the copper uranyl acetate reagent is not nearly so sensitive toward sodium ion as the first four types of reagents listed in Table I, these other reagents are fairly sensitive toward lithium ion, as is shown by Table II. These results were obtained by mixing 5 ml. of a given reagent with 1 ml. of lithium chloride solution and observing the presence or absence of a precipitate at the end of 30 minutes. Though the particular kind of zinc uranyl acetate reagent used in these experiments is slightly less sensitive toward lithium than the magnesium, nickel, or cobalt uranyl acetate reagents, it is also proportionately less sensitive toward sodium. On the other hand, the manganese uranyl acetate reagent is more sensitive to lithium than the copper uranyl acetate reagent, though it has the same sensitivity toward sodium. The copper uranyl acetate reagent appears to be the only practical one that is free from this parallelism in sensitivity toward lithium and

sodium, and for this reason it may be said to be more nearly specific for sodium than any other type of uranyl acetate sodium reagent. However, because it is only moderately sensitive toward sodium ion, it seems to be of more value as a qualitative reagent than as a quantitative reagent.

### Composition of the Potassium Precipitates

All these reagents on being added to concentrated potassium acetate or chloride solutions yield copious crystalline precipitates, but irrespective of the particular reagent employed or of the experimental variations in the volume and concentration of the potassium solutions all such precipitates were found to have essentially the same composition. Only a single type of double salt, a potassium uranyl acetate in which the components are in a 1 to 1 ratio, is formed when these reagents for sodium are added to potassium solutions.

TABLE II. COMPARATIVE SENSITIVITY OF REAGENTS TOWARD LITHIUM

Type of Reagent	20 mg.	10 mg.	5 mg.	4 mg.	3 mg.	2 mg.	1 mg.
Magnesium	+	+	+	+	+	+	—
Nickel	+	+	+	+	+	+	—
Cobalt	+	+	+	+	+	+	—
Zinc	+	+	+	+	—	—	—
Manganese	+	—	—	—	—	—	—
Copper	—	—	—	—	—	—	—
Cadmium	—	—	—	—	—	—	—
Mercury	—	—	—	—	—	—	—

### Precipitation Experiments with Potassium Solutions

After precipitation of 5 ml. of saturated potassium chloride solution with the magnesium uranyl acetate reagent by the general procedure given above, 2.09 grams of air-dried salt were obtained. In a similar experiment with the nickel uranyl acetate reagent the yield was 2.31 grams. Precipitation of 10 ml. of potassium chloride solution containing 100 mg. of potassium per ml. by the addition of the potassium solution to the zinc uranyl acetate reagent produced 2.34 grams of the air-dried salt.

In the analysis of these preparations the uranium was precipitated as ammonium diuranate with carbonate-free ammonium hydroxide and weighed as  $\text{U}_3\text{O}_8$ . After evaporation of the filtrates from the uranium determinations the potassium was converted to sulfate and weighed in this form. Not more than traces of the divalent metals could be detected in any of these preparations. The water content was estimated by difference after calculating the metals to acetates. The results of the analyses are shown in Table III.

TABLE III. COMPOSITION OF PRECIPITATES PRODUCED BY MIXING CERTAIN REAGENTS WITH CONCENTRATED POTASSIUM CHLORIDE SOLUTIONS

Reagent	Sample	Uranium %	Potassium %	Water %
Magnesium uranyl acetate	a	48.53	7.56	1.89
	b	48.48	7.32	2.59
Nickel uranyl acetate	a	48.52	7.44	2.21
	b	48.67	7.52	1.77
Zinc uranyl acetate	a	48.55	7.55	1.79

TABLE IV. THEORETICAL PERCENTAGES OF URANIUM, POTASSIUM, AND WATER REQUIRED FOR POTASSIUM URANYL ACETATES

Formula of Salt	Uranium %	Potassium %	Water %
$\text{KUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$	47.21	7.75	3.57
$\text{KUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	48.06	7.89	1.82
$\text{KUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$	48.96	8.04	..



It is obvious that the same salt is precipitated by all three reagents. The agreement for the uranium and the potassium content of the three preparations is close, though the results for the water content do not agree very well. However, the lack of close agreement in the water content might be ascribed to the method of estimation. If the results in Table III are now compared with the theoretical figures given in Table IV for the uranium, potassium, and water content required by certain formulas for potassium uranyl acetates, it might reasonably be concluded that the precipitate produced in a potassium solution by a uranyl acetate sodium reagent is, in the air-dried state, a hemihydrated potassium uranyl acetate. On the other hand, further experiments demonstrated that the water in such an air-dried precipitate is largely or entirely in the form of hygroscopic moisture.

For example, another preparation produced by precipitating a potassium solution with zinc uranyl acetate reagent and drying the salt to constant weight in air was divided into two samples. The first sample on being dried to constant weight at 100° C. was found to lose 1.54 per cent of water. The second sample on being dried to constant weight at room temperature in a desiccator over phosphorus pentoxide lost 1.60 per cent of water. No change in the form of the crystals in either sample was produced by these methods of drying. That the second sample was free from water after drying was shown by a determination of the uranium and potassium content and a calculation of the total percentage of the components, uranyl acetate and potassium acetate, this being found slightly to exceed 100 per cent. The water content of this particular preparation as shown by these two determinations is below that required by formula for even the hemihydrate.

The water content of air-dried preparations was found to vary according to the humidity of the air at the time of drying, and samples dried over phosphorus pentoxide and then exposed to air differing in humidity absorbed different proportions of water. These experiments indicated that the potassium uranyl acetate precipitated from potassium solutions by sodium reagents is the anhydrous salt, and that this salt is slightly hygroscopic.

An unusual fact about all these preparations of potassium uranyl acetate is the noticeable discrepancy in the ratios of the two components, uranyl acetate and potassium acetate. These ratios as shown by analysis consistently differ from the theoretical 1 to 1 ratio. Thus if the uranyl acetate content of the five samples listed in Table III is taken as unity the proportions of potassium acetate in the same order are 0.95, 0.92, 0.93, 0.94, and 0.95. Though this discrepancy in the ratio might be taken as an indication of the admixture of a small proportion of another double salt in which the ratio of uranyl acetate to potassium acetate is 2 to 1 or higher, the actual reason seems to be that some of the potassium acetate

is preferentially leached out of the salt by the alcohol used for washing, since the discrepancy in the ratio of the components is increased by excessive washing with alcohol. It can similarly be shown that the lithium and sodium triple acetates may also be noticeably decomposed by washing with alcohol. This decomposition of the complex uranyl acetates on being washed with alcohol is significant in explaining some of the differences that have been reported in the determinations of the composition of such salts. This is a source of error that must be considered in the application of such salts in quantitative measurements.

### Summary

The salts precipitated from lithium solutions by uranyl acetate sodium reagents are always triple acetates analogous in composition to the triple acetates precipitated from sodium solutions by these reagents. Though the water content of most of the isolated lithium triple salts is slightly variable, depending upon the conditions of drying, approximately six molecules of water of hydration are present in the salts dried to constant weight at 100–105° C.

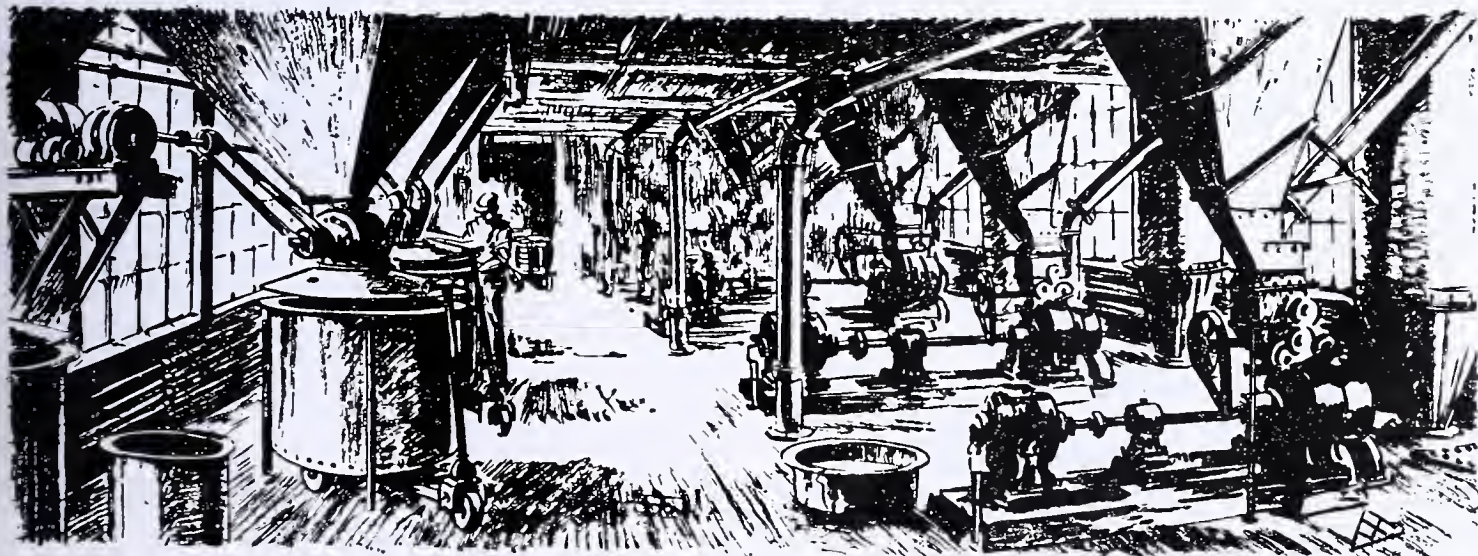
No precipitates were formed in concentrated lithium solutions by the experimental cadmium, mercury, and copper uranyl acetate reagents, and it is doubtful therefore whether the corresponding lithium triple salts exist. It seems certain that such lithium salts cannot be prepared by the method used in this investigation.

The same salt— $\text{KUO}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ —is precipitated from concentrated potassium solutions by all types of uranyl acetate reagents for sodium.

The copper uranyl acetate reagent prepared for use in these experiments appears to be a more nearly specific qualitative reagent for sodium than any other type of uranyl acetate sodium reagent, since it is a moderately sensitive reagent for sodium and yet forms no precipitate with lithium solutions.

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# Analysis of Synthetic Resins Containing Maleic Acid

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FROM an analytical point of view the synthetic resins have not been sufficiently investigated (1, 11). Most work has been done in connection with phthalic acid resins, which are simple alkyd resins, where the phthalic acid has been esterified by a polyhydric alcohol to high molecular compounds. Through saponification phthalic salts are obtained. By acidification the phthalic acid may be obtained in aqueous solution, whereas the oil acids and rosin acids precipitate. From this aqueous solution the lead salt may be precipitated and isolated for determination.

This principle forms the basis of the method of Fonrobert and Münchmeyer (3, 10), and was employed by the author before he knew of these or other publications on the subject.

A more handy method is that of Kappelmeier (4), according to which 0.5 gram of resin dissolved in 5 ml. of benzene is saponified with about 25 ml. of approximately 0.5 *N* potassium hydroxide in *c. p.* ethyl alcohol. In this way potassium phthalate is precipitated with 1 molecule of alcohol. The precipitate is voluminous and needle-shaped. If commercial ethyl alcohol be used as solvent, only a small part can, according to the author's experience, be precipitated, whereas Kappelmeier claims to get sufficient for a technical analysis. After diluting with an equal volume of ethyl ether, the dilution is filtered through a glass filtering crucible, and washed with a mixture of ethyl ether and ethyl alcohol (1 to 1). Thorough washing is necessary, using 50 ml. in some six steps. Thereafter the precipitate is dried in a vacuum and weighed. The salt is very deliquescent.

Other methods have been published by Kavanagh (6) and Kerckow (7).

Although the maleic acid resins belong to the alkyd resins, the question here is more complicated, the maleic acid being combined with the abietic acid according to the diene synthesis. Publications concerning this matter have been compiled by Ellis (2). The configuration of the maleic-abietic acid is given in Figure 1. Before the process, the abietic acid had conjugated double bonds at *x* and *y*, while the maleic acid double bond was at *z*.

An analytical application of this process is the determination of the diene number according to Kaufmann (5) and Sandermann (8). By heating an oil or rosin with an excess of maleic anhydride in a suitable solution, and after treatment and separation of the excess maleic acid titrating this excess or the adduct, the conjugated double bonds can be determined.

Of maleic-abietic acid, a considerably more hydrophilic character is to be expected than of the other resinous products. At least some solubility in water should be expected, as well as an insoluble lead salt. A series of investigations based on these assumptions resulted in the procedure reported below.

## Procedure

One-fifth gram of resin is dissolved in 5 ml. of benzene and saponified with 20 ml. of *N* potassium hydroxide in 90 per cent ethyl alcohol with a reflux condenser for an hour in a 100-ml. Erlenmeyer flask, followed by heating for half an hour without a condenser in a steam bath. Fifty milliliters of water are added to the residue, and the flask is again left for half an hour in the steam bath. The material is transferred to a 300-ml. Erlenmeyer flask and water added to a volume of 200 ml. Using methyl red as an indicator, approximately 6 to 7 ml. of 4 *N* acetic acid are

added until the color approaches red. As the precipitated rosin is red in color, the dispersion will appear red, even though the liquid is orange. The precipitate therefore must settle before the color is observed; pH about 4.5. The material is filtered and washed twice, and as a smell of hydrogen sulfide often is noticed, boiled for 10 minutes. Next it is precipitated with 5 ml. of 1 to 10 lead acetate solution. The result is a flocculated colloidal precipitate, which, after cooling, is filtered through a Jena glass filtering crucible (10 G 4). Including the washings, the filtration will take about 2 hours, as the precipitate is sticky and the pores of the filter become clogged. The precipitate is dried for 45 minutes at 80° to 90° C. and weighed. The factor for the maleic acid-lead precipitate is approximately 0.30, assuming that 60 per cent of the maleic acid used in the resin is found by this procedure.

On heating the precipitate with dilute hydrochloric acid the maleic-abietic acid separates as a resinous lump, while phthalic and similar acids will dissolve.

The filtering crucible is best cleaned with alcoholic alkaline solution.

## Precision

How carefully the various operations have to be performed will be obvious from the following.

If a double sample of resin is precipitated in half the solvent, the resulting precipitate is about one third of the above-mentioned. Roughly speaking, this applies to samples of both 10 and 20 per cent maleic acid. The conclusion must be that the maleic-abietic acid is divided between the water phase and the precipitated rosin. If the material contains only a small amount of maleic acid, and consequently but a small amount of maleic-abietic acid, the comparatively large quantity of rosin will absorb some maleic-abietic acid. If on the contrary much maleic-abietic acid and but little rosin are present, the rosin will absorb only a small quantity of maleic-abietic acid. The more free rosin present, the further must the aqueous solution be from saturation in order that the same percentage of maleic-abietic acid may be found present. If 0.1 gram is taken, practically the same percentage is found as with 0.2 gram. Consequently the lead precipitate is sufficiently insoluble not to demand special precautions, while the method has to be based upon the slight solubility of maleic-abietic acid.

If the sample is saponified for 15 minutes with 0.5 *N* potassium hydroxide solution, evaporated for 10 minutes in a steam bath, and transferred to cold water, the precipitate will be about one-

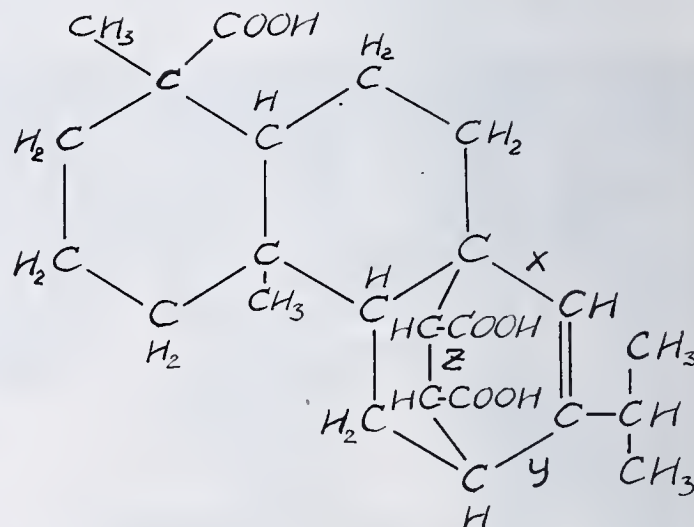


FIGURE 1. MALEIC-ABIETIC ACID  
 $C_{24}H_{34}O_6$ , molecular weight 418



half that which is found when the above procedure is followed. If the resin is saponified for 4 hours and the aqueous solution is left for 4 hours in a steam bath, about five-sixths will be found. As the maleic-abietic acid to a great degree will be dehydrated, even if maleic acid is used as in the author's experiments, instead of maleic anhydride as in common manufacture, the object of the saponification is also hydration; consequently the treatment with alkali is continued in aqueous solution in the steam bath.

If acidification is effected through a 10-ml. excess of 4 *N* acetic acid, so that the resulting mixture is about 0.2 *N* as to acetic acid, the precipitate will be approximately one-fourth of the percentage according to the procedure. If only the rosin is precipitated at this acidity, while the acidity is adjusted to pH 5 before the lead precipitation, one-fourth is also found. This proves that the sensitive point is the rosin precipitation (6), while the lead precipitation is not influenced by this slight acidity.

In every case 1 ml. of 1 to 10 lead acetate solution will be stoichiometrically sufficient. If the double quantity is used, this will hardly be sufficient for a quantitative precipitation; 5 ml. are enough in every case and do not require accurate measuring.

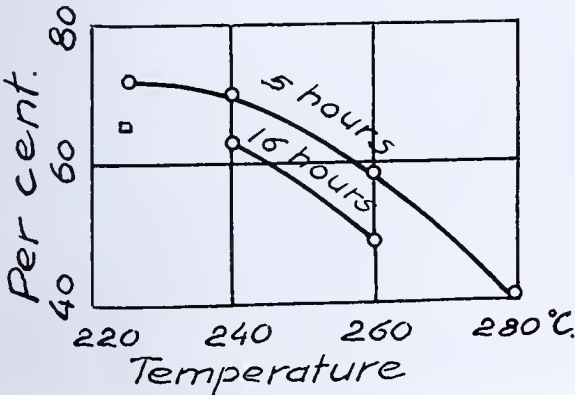


FIGURE 2. RELATION BETWEEN MALEIC ACID FOUND AND TEMPERATURE OF TREATMENT

When analyzing a synthetic varnish the precipitate from the acid precipitation may, on account of fatty acids, be too liquid for a filtration. In this case it may be shaken with 100 ml. of benzene, the benzene shaken with 50 ml. of water, and lead acetate added to the combined water fractions. The resulting precipitate will not be essentially below that of the above procedure. The benzene, however, will be dispersed in the aqueous solution, so that a distinct separation will be tedious.

The free maleic acid will not precipitate; 0.2 gram is the limit and 0.05 gram (maximum in 0.2 gram of resin) will certainly not precipitate from an aqueous solution, to which 4 *N* sodium hydroxide is added until the pH value is 4.5. With the quantities of potassium acetate present with this procedure, the dissociation of the lead acetate is decreased, so that the possibility of precipitation is even less.

With this knowledge of the method a reproducibility of 2 per cent may be attained. The other constituents of the resin, however, will influence the result, especially the products formed by a vigorous treatment.

Accuracy

The lead precipitate is heated with concentrated sulfuric acid (9) and transformed to lead sulfate. Computed as a tertiary salt, (C<sub>24</sub>H<sub>31</sub>O<sub>6</sub>)<sub>2</sub>Pb<sub>3</sub>, on the average 84 per cent will be found—in exceptional cases below 80 per cent or over 90 per cent. Computed as a secondary salt, C<sub>24</sub>H<sub>32</sub>O<sub>6</sub> Pb, 108 per cent is also the average. Consequently the lead precipitate apparently consists of 33 per cent tertiary salt and 67 per cent secondary salt. The factors are:

Tertiary lead maleic-abietate:lead sulfate = 1.60  
Secondary lead maleic-abietate:lead sulfate = 2.05

For computation of the precipitated lead salt as maleic acid, we have the factors:

Maleic acid:tertiary lead maleic-abietate = 0.160  
Maleic acid:secondary lead maleic-abietate = 0.186

If the average composition of the precipitated lead salt is computed as above, we have the factor 0.177. Using this factor there is found on the average 60 per cent of the quantity of maleic acid used in the resins, the least in strongly processed products, the most in less processed ones.

In the curves of Figure 2 the percentage of maleic acid found is plotted against the highest temperature at which the resins were treated. In the upper curve the temperature was kept constant for 5 hours, in the lower one for 16 hours.

TABLE I. CONDITION OF MALEIC ACID DURING TREATMENT

Sam- ple No.	Treat- ment Time Min.	Tempera- ture ° C.	Acid No.	Tertiary Lead Maleic- Abietate in Frac- tion 1 %	Total Frac- tion 1 %	Maleic Frac- tion 2 %	Acid Frac- tion 3 %	Sum of Three Frac- tions	Free Maleic Acid %
I	10	180	221	83	80.5	12.2	2.4	95.1	1.9
II	30	180	221	..	77.5	6.2	3.1	86.8	1.8
Hours									
III	1	180	212	85	72.6	12.8	3.6	89.0	1.4
IV	5	225	200	85	72.4	7.9	4.2	84.5	0.5
V	14	260	36	83	57.4	9.9	3.3	70.6	0.05
VI	22	260	31	85	48.6	5.2	1.3	55.1	...

By the treatment the temperature was by steps brought up to this maximum. Some of the products are esterified, some not. The maleic acid content was between 10 and 18 per cent. The values are not influenced by these variations; on the contrary, a resin that contained 26.2 per cent of maleic acid, corresponding to 94.5 per cent of maleic-abietic acid, falls outside the curve and is plotted as a square. This was to be expected, as the total quantity of acid in a rosin is not present as indicated in Figure 1, and as maleic-abietic acid only can be formed when the conjugated system is present (2).

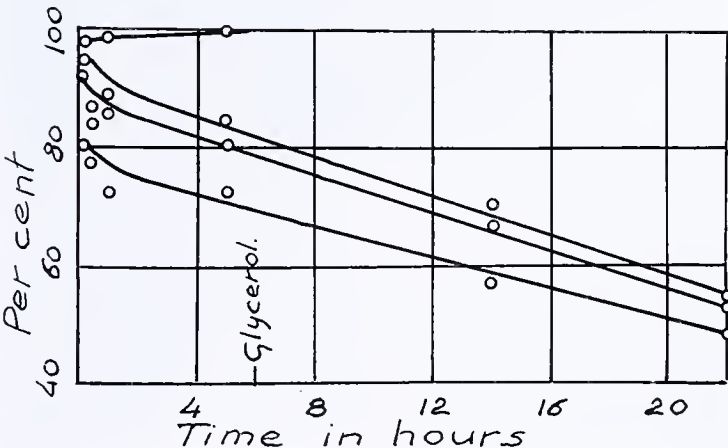


FIGURE 3. RELATION BETWEEN MALEIC ACID FOUND AND TIME OF TREATMENT

In order to account for the total quantity of maleic acid, the experiment represented in Table I and Figure 3 was conducted. Before the esterification this resin contained 15.1 per cent of maleic acid and after esterification 14.2 per cent, being prepared from 900 rosin, 160 maleic acid, and esterified with 210 glycerol containing 12 per cent of water. In the computation due regard is paid to the water content of the glycerol, the water formed during esterification, and half of the water which would disappear through complete dehydration of the maleic acid used. From the acid numbers it will be evident that about one half of the maleic acid is dehydrated. The theoretical acid number of the mixture is 284. If the



maleic acid is dehydrated the figure will be 140. The author used an American rosin with an acid number of 161 and an iodine number of 137 (Hanus reagent, solution in carbon tetrachloride, 2 hours' standing). The acid number of maleic acid is computed as 968, its iodine number being 0.

The iodine numbers approach 90, a value corresponding to one double bond in maleic-abietic acid, and two in the remaining abietic acid. Before the esterification the maleic-abietic acid is computed at 54.8 per cent.

Other products, where the acid numbers have fallen comparatively more, show iodine numbers lower than those corresponding to a single double bond.

In Table I the second column indicates the time from the moment the total quantity of maleic acid is added to the rosin.

Where the temperature increases, the increase is made during the first hour.

Esterification with glycerol was made one hour after sample IV was taken out. According to theory, the acid number should fall to 0, as 10 per cent more glycerol was added than that corresponding to complete esterification.

A lead determination in the lead precipitates is computed as percentage of tertiary lead maleic-abietate, and the results are recorded in column 5. The corresponding average factor is used for computing the quantity of maleic acid indicated in column 6 as fraction 1. The computation is made as follows:

$$\frac{\text{Weight of lead precipitate} \times \text{average factor (0.177)} \times 10,000}{\text{Weight of sample} \times \text{percentage maleic acid used in resin}}$$

The maleic acid in the precipitates recorded as fractions 2 and 3 is computed against another factor as explained below.

The rosin acids isolated through filtration were again dissolved on the filter with the same quantity of alcoholic potassium hydroxide that was applied in the procedure proper, using more ethyl alcohol to wash the filter. This quantity of potassium hydroxide is not necessary for solution of the precipitate, but if the corresponding quantity of potassium acetate is not present at the precipitation of the acids, the rosin acids will not coagulate in a state fitted for filtration. Furthermore, the buffer action is necessary to regulate the hydrogen-ion concentration. The material is transferred to water and precipitated once more exactly as before. Only the cooking before the lead precipitation may be left out. The result is shown as fraction 2.

The procedure is repeated the third time to give fraction 3.

All these small precipitates (fractions 2 and 3) were treated with concentrated sulfuric acid, and gave 78 per cent tertiary or 100 per cent secondary lead maleic-abietate. The maleic acid in these fractions was calculated with the corresponding factor. Less lead is to be expected in these fractions, as the higher processed compounds probably also are precipitated as lead salts to some degree.

That fraction 2 seems erratic must be due to the great sensibility of the precipitation towards the hydrogen-ion concentration. If fraction 1 is precipitated in too acidic solution, it will be too small, and what is missed is found in fraction 2. In Figure 3 curves are plotted for percentage of maleic acid in fraction 1, 1 plus 2, and the total of all three fractions against the time of treatment. The plotted values distribute themselves almost to the same degree around the three curves.

For a determination of the total quantity of maleic acid, found as maleic-abietic acid by a computation of the quantity in fraction 1, we have the factors:

Sum of fractions : fraction 1 = 1.175

Maleic acid as maleic-abietic acid: fraction 1 = 0.208

The free maleic acid was arrived at by shaking 5 grams of resin dissolved in 50 ml. of benzene with 25 ml. of water. By way of control, 5 grams of rosin, also in 50 ml. of benzene, were shaken with 25 ml. of water in which 0.1 gram of maleic acid had been dissolved, and 50 ml. of benzene were shaken with 25 ml. of water in which 0.1 gram of maleic acid also had been dissolved. The shaking was done in a machine for a couple of hours, so that the maleic-abietic acid might find its equilibrium between the two phases. The 0.5 per cent found in sample IV corresponds to the quantity of maleic-abietic acid anticipated to be found in the water according to the above statements. Whether or not it corresponds to a blank is unimportant. The free maleic acid is hereafter below 2 per cent in sample I and decreases rapidly. It is determined through titration of the

aqueous solution with 0.1 *N* sodium hydroxide, using phenolphthalein as an indicator.

In Figure 3 the free maleic acid is plotted downwards from the upper horizontal axis. In the interval between free maleic acid and maleic acid as maleic-abietic acid, combinations will be found, not reported here.

Immediately after beginning the experiment the author found 95 per cent of the maleic acid as maleic-abietic acid and 2 per cent as free maleic acid. No better result can be expected, considering that great quantities reacted further during the process, and that the addition of the maleic acid to the rosin required 2 hours.

### Specificity

With this procedure colophony gives no lead precipitate; neither do the phenol-formaldehyde resins. The phthalic acid resins, however, form a crystalline precipitate, easily distinguished from that of maleic-abietic acid (3). The phthalic acid may be removed, when the saponification is made according to Kappelmeier (4); then the potassium phthalate is separated by filtration, the filtrate transferred to water, and saponification continued in aqueous solution in a steam bath for an hour.

If, on the contrary, the maleic acid resins are saponified according to Kappelmeier's method, a colloidal precipitate is obtained, amounting to some few per cent of the resin, which is easily distinguished from the voluminous potassium phthalate. The precipitate may first be formed by the addition of ether after the saponification. If phthalic acid is found, a few per cent of the maleic acid, if any, will follow the phthalic acid. If phthalic acid is not found, the small colloidal precipitate should not be isolated by filtration, but simply transferred to water together with the solution.

### Summary

The literature contains no methods for the chemical analysis of maleic acid (anhydride) resins, but mentions the fact that such do not exist.

Considerations based on new theories regarding the constitution of these (the diene synthesis) have led to the method described above.

What has been utilized analytically is a chemical property: solubility in faintly acidic aqueous solution. This proves to be typical for maleic-abietic acid, as contrasted with the constituents of rosin and phenol-formaldehyde resins, while phthalic acid from phthalic resins may be removed in advance.

A quantitative determination of maleic-abietic acid is obtained. Its quantity is reduced during the production of resin from approximately 100 per cent to an average of about 60 to 70 per cent. The method may be employed as a control of the process, and to give an idea of how much maleic acid enters into an unknown resin, at least serving for its identification.

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# Determination of Soybean Flour in Sausage by Nonfermentable Sugars

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ALTHOUGH much has been published in regard to the soybean's diversity of uses and the value of edible soybean flour as a low-cost source of protein, fat, calcium, phosphorus, and iron in the human diet (9, 23), soybean flour has not yet attained appreciable retail distribution and, like any new food product, probably will not until after long and expensive consumer education. It is, however, reaching the public to a limited extent in certain manufactured food products, such as sausage and related meat products.

Federal regulations have long permitted the properly declared addition of cereal products up to 3.5 per cent in sausage. These materials are useful in binding the natural moisture content of the meat and in improving the texture and firmness of the product. The amount of cereal flour used can be readily controlled by determination of the kind and amount of starch present. Soybean flour is also a very effective binder in sausages and furthermore does not lower the protein content, since it contains twice as much protein as lean meat. However, the regulations of the Bureau of Animal Industry do not at present permit the use of soybean flour in meat products made in federal-inspected plants, on the sole ground that there is no quantitative method of determination and hence no method of check on the amount used. Accordingly its use is confined to intrastate business, where it is frequently restricted because of adoption of Bureau of Animal Industry regulations by local inspection authorities.

## Qualitative Tests

These prohibitions can be readily enforced because effective qualitative tests for soybean flour are available. One depends on the liberation of ammonia from urea by the urease of the soybean (16, 18). This sometimes fails because the urease has been inactivated by the "debittering" process (usually involving some form of steaming) applied to all edible soybean flours to make them acceptable to the American taste or by the cooking applied to certain types of sausage in manufacture. One method, which is based on obtaining a residue of hemicellulosic material by insolubility in alcoholic potassium hydroxide and microscopic identification in this residue of the typical spool-shaped subepidermal cells of the soybean, seems reliable (16, 25). A serum precipitin test has also been described (27).

## Bases for Quantitative Method

Soybean flour contains no starch; therefore some other basis for analysis must be sought. As the major and least variable constituents are protein and nonstarchy carbohydrates, one or both of these materials would seem to be the logical basis for a method of identification. The characteristic protein, glycinin, is specific for the soybean and, as it comprises about 50 per cent of the flour, seems an ideal basis for an analysis. However, this protein will be present in a large excess of meat proteins and its solubility properties vary with the amount of denaturation resulting from the various debittering processes and sausage preparation methods. Furthermore, a general method must also apply in the presence of a wide variety of possible accompanying materials, such as cereal proteins, liver, dried milk proteins, etc. An attempt by a commercial laboratory to develop a reliable chemical separation of the soybean protein, supported by the Soybean Processors Association and extending over about 3 years, has so far not been successful (17).

Recently a preliminary report has appeared on a promising method by which the soybean protein in sausage is determined biologically by means of a quantitative modification of the rabbit serum precipitin reaction (14). This method is now being further studied to determine its applicability to soybean flours of various preliminary histories (13).

A method which has been proposed for controlling the total amount of soybean flour and other carbohydrate-containing materials added, is based on the indirect determination of "nitrogen-free extract" which is essentially zero for meat but common to all carbohydrate-containing materials (15).

## Reducing Sugar Method

Meanwhile the present author developed a direct carbohydrate method based on hydrolysis to reducing sugars and determination of the latter with Fehling's solution. It has been found possible to impart a considerable degree of specificity to this method by taking into account the particular nature of the carbohydrates of soybean flour and basing the determination on insoluble, nonfermentable sugars present, using a quick and convenient fermentation technique. This procedure eliminates interference from soluble sugars, starch, modified starch, and glycogen, which are the carbohydrate materials most apt to accompany soybean flour in meat products. Serious interference will be shown by materials high in pentosans, arabans, etc., such as whole-wheat flour, but such products are not normally added to sausages. The method appears to give results sufficiently accurate for control purposes. Although further experience will doubtless permit additional refinements, the author, not being directly concerned with analysis of meat products, is not in position to pursue the study further and therefore it seems advisable to present the method as so far developed.

Little work has been done to determine the particular carbohydrates present in soybeans or soybean flour. Fairly complete group analyses have been reported by Street and Bailey (24) and by Yukawa, who is quoted by Sato (21) as authority for the following analyses of the soybean:

	%		%		%
Total carbohydrates	21.69	Stachyose	3.52	Galactan	4.62
Sucrose	5.90	Araban	3.80	Crude fiber	3.82

After trying various procedures based on converting galactans to mucic acid, converting pentosans to furfural, utilizing the residue insoluble in alcoholic potassium hydroxide, and various methods of hydrolyzing the hemicelluloses to reducing sugars and distinguishing the soybean sugars from those derived from extraneously added dextrose, sucrose, starch, and lactose, by diastase, optical rotation, fermentation, etc., the procedure below was adopted. Although the procedure as given includes determinations of soluble and insoluble sugars, only the determination of nonfermentable sugars, is required to determine the presence of soybean flour. The other determinations are used only in case information is desired concerning added sugars and starches.

## Method A. Insoluble Nonfermentable Sugars

1. PREPARATION OF SAMPLE. Take samples containing about 2 grams of soybean flour (50 grams of unknown sausage). Prepare samples as directed by the Association of Official Agricultural Chemists (5). (Grind, evaporate two or three times with 95 per cent alcohol, extract most of the oil with petroleum ether,



TABLE I. SOYBEAN FLOURS USED

Expt. No. Type	212 Expeller (de- hulled)	189 Expeller (whole beans)	211.1 Expeller	211.2 Aqueous (de- bittered)	208.2 Unknown
Moisture, %	4.10	6.35	3.80	6.00	6.50
Ash, %	5.62	5.31	5.62	3.31	5.80
Protein, %	52.15	45.86	48.67	67.15	46.38
Oil, %	5.88	6.09	8.63	4.40	3.94
Crude fiber, %	2.36	4.99	2.40	2.60	6.41
Nitrogen-free extract (by difference), %	29.89	31.40	30.88	16.54	31.15

TABLE II. GROUND MEAT AND DRIED AND DEOILED MEAT POWDERS USED

Expt. No. Description	193.1 <sup>a</sup> Ground lean pork and beef	193.2 193.1 dried and deoiled	194.2 Like 193.2	207 Like 193.2
Moisture, %	73.34	26.29	4.83	2.01
Ash, %	0.93	...	...	...
Protein, %	22.50	...	67.85	84.44
Oil, %	4.00	1.11	1.60	7.86
Crude fiber, %	None	...	...	...
Nitrogen extract, (by difference), %	-0.23	...	...	...

<sup>a</sup> 217 and 218 like 193.1.

and regrind.) Filter the petroleum ether extract through the same filter paper as used under (2).

2. REMOVAL OF WATER-SOLUBLE SUGARS. Place the weighed samples in iodine number flasks and wash by decantation with neutralized 50 per cent alcohol, pouring the liquid through an 11-cm. No. 42 Whatman filter paper coated with 0.3 cm. (0.125 inch) of washed Filter-Cel. Transfer most of the solid to the paper and wash five times more with the 50 per cent alcohol. Total washings should amount to about 200 cc.

3. DETERMINATION OF SOLUBLE SUGARS (OPTIONAL). The amounts of added sugars may be determined by treating the filtrate as directed (2) starting with "evaporate on a steam bath to 20 to 30 cc.", and (3), but using the inversion conditions of (4) instead of (3). Reducing sugars obtained from commercial soybean flours before inversion are usually negative or so small as to be negligible, while sugars after inversion range from 2.12 per cent (one sample) to 12 to 14 per cent invert sugar (11.5 to 13.5 per cent as dextrose).

4. DETERMINATION OF INSOLUBLE SUGARS. Transfer the washed residue and Filter-Cel, after drying a short time to expel most of the alcohol, to the original iodine number flask, and add 120 cc. of 2.5 per cent hydrochloric acid from a small wash bottle, washing the paper and sides of the flask. [Sulfuric acid hydrolysis followed by barium hydroxide neutralization assists clarification and reduces the salt content of the solutions but hydrolysis is somewhat less complete. Hydrochloric acid was also found more effective on rice bran hemicelluloses by Fukagawa and Ri (12) and by Yanovsky (26).]

Provide the flask with rubber-stoppered reflux air condensers and hold in a boiling saturated salt bath for 3 hours. Nearly neutralize with 10 per cent sodium hydroxide (alkaline to methyl orange and acid to litmus), transfer to a 250-cc. volumetric flask, make nearly to volume with hot water, add 2 cc. of 50 per cent phosphotungstic acid, shake, and allow to cool to room temperature. Make to volume, shake, and centrifuge or filter. Pipet 200 cc. of centrifugate to a 250-cc. volumetric flask, add 30 cc. of 50 per cent phosphotungstic acid solution, make to volume with water, shake thoroughly, and centrifuge. Test for complete precipitation with a crystal of phosphotungstic acid. Pipet 200 cc. into a 250-cc. volumetric flask, and add dry potassium chloride in slight excess to precipitate excess phosphotungstic acid. (If no precipitate forms add 1 to 2 cc. of phosphotungstic acid solution.) Add 1 drop of methyl orange solution and neutralize to methyl orange and litmus. Cool, make to volume, shake, and filter through dry No. 42 Whatman paper. If desired, determine per cent of insoluble sugars by the A. O. A. C. method (7) on an aliquot. (For soybean flour this figure will be about 11 to 12 per cent of invert sugar or 10.5 to 11.5 per cent of dextrose.) [See (6) in connection with the preparation of the solution for sugar analysis. If total insoluble sugars are determined at this point, the amount of starch present may be calculated approximately from the difference between total insoluble sugars and nonfermentable insoluble sugars. Soybean flour shows about 2 per cent (invert sugar), insoluble fermentable sugars.]

5. DETERMINATION OF NONFERMENTABLE SUGARS. [This quick fermentation method is adapted from Bailey (8), who used

it to determine lactose in frankforts, from Somogyi (22), and others. According to Somogyi, less than 10 minutes is necessary to remove dextrose completely while over 30 minutes causes removal of maltose, etc. Fermentation time does not seem very important with soybean flour, but the 45-minute period appears to give slightly better results than shorter times. The method seems to rest on adsorption rather than fermentation (20). Toluene may be added to preserve the solutions, if desired, without hindering the removal of "fermentable" sugars. The older method of 3- to 5-day fermentation (1) caused practically complete destruction of the sugars.]

*Preparation of yeast.* Wash fresh bakers' yeast five times by stirring up with three times its volume of distilled water and centrifuging. The last washing should be clear. Keep 25 per cent suspension in water at about 0° C. Prepare fresh at least once a week.

*Fermentation.* Place 10 cc. of the yeast suspension in a 100-cc. centrifuge tube, centrifuge, pour off water, and dry inside of tube with filter paper. Add about 60 cc. of the sugar solution from (4) through a funnel (first diluting, if necessary, to contain not over 0.1 per cent concentration of fermentable sugars). Stir up the yeast well and let stand 45 minutes, preferably at 30° C. Stir up once more during this period. Centrifuge and filter through a dry No. 42 Whatman paper. Analyze for per cent of invert sugars by the A. O. A. C. method (7). Control tests on the yeast activity should be run on 0.1 per cent dextrose solutions. The dextrose should be completely removed.

## 6. CALCULATION OF RESULTS.

$$\% \text{ nonfermentable sugars in sample} \times 9.4 = \frac{\% \text{ soybean flour in sample}}{\% \text{ nonfermentable sugars in sample}}$$

TABLE III. ANALYSES OF SOYBEAN FLOURS BY METHOD A

Expt. No. No. of flour Type	212.1 212	205.1 189	208.1 208.1	208.2 208.2	211.1 211.1	216.2 211.2	216.4 Mohican brand corn- starch
Soluble sugars as % invert sugars	11.80	11.65	13.83	14.25	14.94	2.12	...
Insoluble sugars as % invert sugars	11.48 <sup>a</sup>	12.50 <sup>a</sup>	11.43 <sup>a</sup>	12.63 <sup>a</sup>	13.32 <sup>a</sup>	12.42	98.91
Insoluble sugars after fermentation	9.34	10.05	9.27	9.87	10.04	10.31	0.34
	9.34	10.15	9.22	9.87	9.69	10.31	0.00

<sup>a</sup> Filter paper included in HCl hydrolysis. This was found to increase the % sugars by about 10 mg. of dextrose (0.5% in most of above cases) and hence was discontinued. The figure for sugars after fermentation is not affected.

TABLE IV. METHOD A ON GROUND MEAT AND MEAT POWDERS

Expt. No. No. of sample Description	205.2 193.2 Powder	210.3 207 Powder	217.1 217 <sup>a</sup> Ground meat	218.1 218 <sup>a</sup> Ground meat
Soluble sugars as % invert sugars	0.00 <sup>b</sup>	0.35	0.045	0.198
Insoluble sugars as % invert sugars	1.31 <sup>c</sup>	1.40	0.062	0.204
Insoluble sugars after fermentation	0.00	0.052	0.009	0.0036
	0.00	0.102	0.018	0.0075

<sup>a</sup> Like No. 193.1. <sup>b</sup> Not hydrolyzed. <sup>c</sup> Filter paper included.

TABLE V. METHOD A ON KNOWN MIXTURES WITH SOYBEAN FLOUR

Expt. No. Composition, %:	214.1	217.2	214.3	214.5a	214.5b
Soybean flour	4.0	4.762, No. 212	4.0, No. 208.2	3.0	5.82
Ground meat	96.0	95.238	96.0	96.0	92.25
Modified starch	....	....	....	0.9	1.74
Dextrose	....	....	....	0.1	0.19
Found:					
Soluble invert sugars, %	0.53	0.64	0.66		
	0.58	0.48	0.57	0.51	0.97
Insoluble invert sugars, %	0.49	0.733	0.59		
	0.51	0.817	0.57	1.21	2.26
Insoluble sugars after fermentation (D), %	0.400	0.508	0.43		
	0.389	0.532	0.40	0.32	0.63
Calcd. soybean flour (10 × D), %	3.95	5.2	4.15	3.2	6.3
Error, %	-0.05	+0.44	+0.15	+0.2	+0.48
Corrected soybean flour (9.4 × D), %	3.72	4.9	3.9	3.0	5.9



TABLE VI. METHOD B, DIRECT HYDROLYSIS

Expt. No. Sample	212.3 Flour 212	213.1 Meat powder 207	217.3 Ground meat 217	214.2 4% flour 212, 96% ground meat	214.4 4% flour 208.2, 96% meat	210.2 15.0% soybean flour 4.5% modified starch 0.5% dextrose 80.0% meat powder 207
Total sugars as invert sugars, %	23.63 23.56	1.89 1.99	0.525 0.506	1.21 1.30	1.32 1.26	10.82 10.48
Nonfermentable sugars as invert sugar, (C) %	14.30 14.45	0.55 0.42	0.208 0.208	0.65 0.68	0.68 0.66	2.38 2.35
Calculated soybean flour (C/0.144), %	...	..	...	4.6	4.7	16.4
Error, %	...	..	...	+0.6	+0.7	1.4 <sup>a</sup>
Corrected soybean flour (C - 0.10)/1.44, %	...	..	...	3.92	3.95	15.7

<sup>a</sup> Converted to 22.5% protein basis  $(1.4 \times \frac{84.0}{22.5})$  this error would be +0.37%.

Experimental Results

Table I gives data on the representative commercial soybean flours used. These are all low-fat flours such as are used in meat products, and in manufacture all have passed through a deoiling and a debittering process. Sample 211.2 was debittered with dilute sulfur dioxide solution which markedly altered its composition. Surprisingly enough, even this flour falls fairly well in line by the analytical method described.

Table II gives similar data on the meat samples used in making up the knowns. All samples consisted of equal parts of lean beef and pork muscle.

Table III gives data obtained on the soybean flours by Method A. The figures for soluble sugars and insoluble sugars are included as a matter of interest although they do not enter into the calculation of soybean flour. They may be used if it is desired to determine added starches and sugars simultaneously with the soybean flour. The unusual composition of sample 211.2 has been commented on above. Sample 216.4 shows the virtually complete absence of interfering materials in commercial edible cornstarch. Table IV shows that only very small amounts of interfering substances are obtained from the meat itself.

Table V shows that results for known mixtures accurate enough for control work are obtained by using the representative factor of 10.0 per cent for soybean flours. With the one exception shown, these and other determined values are somewhat high, showing that allowance should be made for the small blank correction for the meat and for the volumes occupied by the precipitates in the aliquot procedure used. Not enough data are yet available to determine the extent of these corrections with much confidence, but it can be seen that the corrected factor 9.4 gives close agreement with the correct values.

Short Method

The two reasons for washing the sample with 50 per cent alcohol are to remove unfermentable lactose if present and to remove most of the nonfermentable reducing substances derived from the meat itself. Lactose could be tested (16) for and determined (8) separately if present and a correction for this and for a blank meat determination applied to total nonfermentable sugars. This would provide no simplification, however. If lactose is absent a considerably shorter procedure omitting the washing step can be used, as shown under Method B which is advanced only tentatively at present, since not enough data are available to determine the general validity of the blank correction.

Method B. Total Nonfermentable Sugars

Weigh 50-gram ground samples of sausage into iodine number flasks and hydrolyze as under A-4. After hydrolysis and neutrali-

zation, extract most of the fat from the solution by shaking up with petroleum ether three times and removing the latter with a pipet. Wash the petroleum ether extract once with a small amount of water and add the water to the hydrolyzate. Heat briefly to expel traces of solvent and proceed as under A-4 and A-5.

$$\frac{\% \text{ nonfermentable sugars}}{0.144} =$$
$$\% \text{ soybean flour (uncorrected)}$$

Representative data determined by this method are given in Table VI. The uncorrected errors are somewhat higher;

hence Method A is favored at present. The chief cause of the higher results by Method B lies in the nonfermentable reducing substances derived from the meat itself. These are probably not all true sugars (11). Further experience with the method should enable a satisfactory correction factor based on the protein content of the sample to be worked out. Apparently this will be smaller than the factor obtained by blank determinations on meat. This may be due to promotion of the fermentative removal of these materials by the presence of an excess of fermentable sugars (10, 19). Trial application of the correction factor of 0.1 per cent invert sugars is shown in the last line of Table VI.

Acknowledgment

Valuable assistance was given by other members of the laboratory staff, especially Jean Constable who made all the sugar determinations.

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# Quantitative Determination of Aromatic Hydrocarbons by New Method

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A simple method has been developed for the rapid quantitative determination of aromatics in hydrocarbon mixtures boiling in the gasoline and naphtha range.

The method is a purely physical one and is based on the measurement of the specific dispersion of the sample. The dispersion is measured on an ordinary Abbé or, where more accurate results are desired, on a Pulfrich refractometer.

The theory underlying the method has been checked on a number of synthetic mixtures.

**S**IMPLE and accurate methods for the determination of aromatics in hydrocarbon mixtures have always been desirable, but they become particularly so in view of the rapid development of hydrocarbon chemistry in the last few years.

The method described here is a purely physical one that consists essentially in determining the specific dispersion of the hydrocarbon mixtures. In contrast to the chemical or physicochemical methods, it is not necessary to remove the aromatics from the mixture. As herein described, the method is limited to aromatic hydrocarbons boiling below naphthalene (219° C.) and covers the boiling ranges of gasolines and naphthas. In principle the method of specific dispersion analysis may be applied to nonhydrocarbon material.

A critical discussion of the advantages and disadvantages of other methods suggested for the determination of aromatics and a comparison with the present one will be reserved for a subsequent publication.

## Principle of the Method

As is well known, the dispersion,  $\Delta$ , of a substance is the numerical difference in the indices of refraction for two specified wave lengths. The specific dispersion,  $\delta$ , is the dispersion,  $\Delta$ , divided by the density,  $d$ , both taken at the same temperature. For practical purposes, it is convenient to use the  $H_\alpha$  (6563 Å.) and  $H_\beta$  (4861 Å.) lines and multiply by the factor 10,000. The specific dispersion,  $\delta$ , at the temperature,  $t$ , is thus defined by means of the expression

$$\delta' = \frac{n'_{H\beta} - n'_{H\alpha}}{d'_4} \times 10^4$$

As a standard temperature, in line with other physical-chemical constants, the temperature 20° C. has been chosen. In the authors' tables the dispersion,  $\Delta_{H\beta} - H_\alpha$ , is also multiplied by the factor  $10^4$ .

The authors' method of analysis is based on the fundamental fact, established particularly by Darmois (1) in 1920 and further developed by Waterman and Perquin (12), Ward and Fulweiler (10), Fuchs and Anderson (3), and Ward and Kurtz (11), that all saturated hydrocarbons, paraffins, or naphthenes, either mono- or polycyclic, independent of their molecular weights, have a practically constant specific

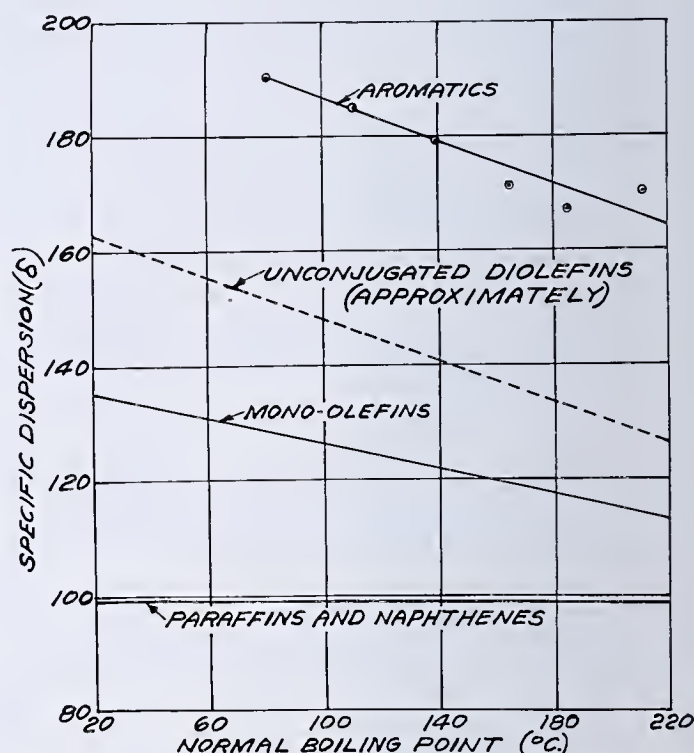


FIGURE 1. SPECIFIC DISPERSION vs. BOILING POINT FOR VARIOUS HYDROCARBON CLASSES

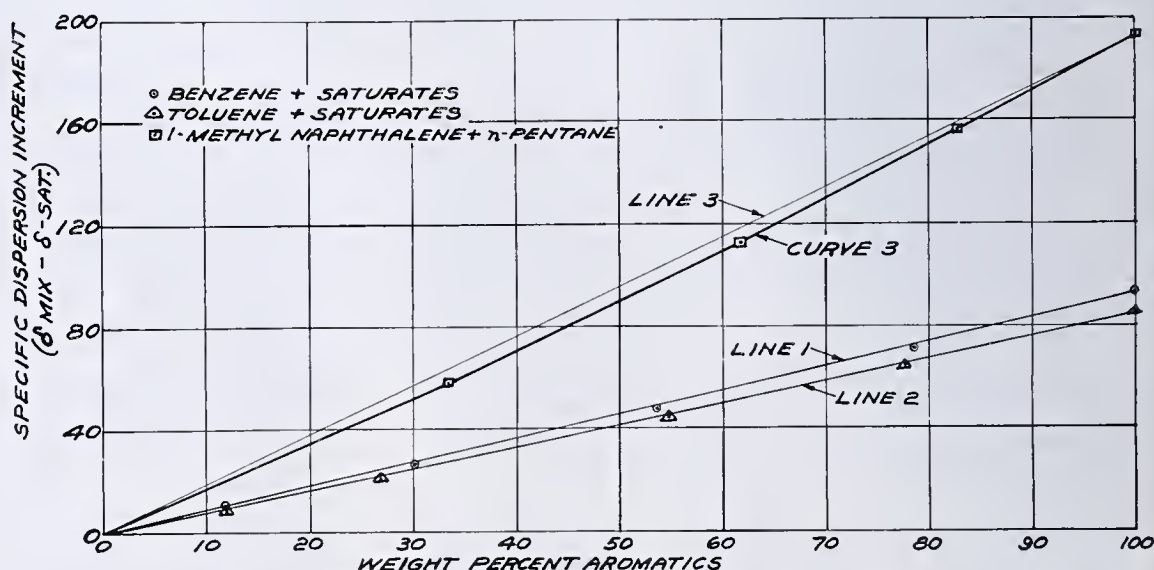


FIGURE 2. SPECIFIC DISPERSION vs. CONCENTRATION IN MIXTURES OF AROMATICS AND SATURATES



TABLE I. UNPUBLISHED DATA ON DISPERSION AND SPECIFIC DISPERSION OF HYDROCARBONS<sup>a</sup>

	Temp. ° C.	$d_4^t$	$n_D^t$	$n_{H\beta}^t$	$n_{H\alpha}^t$	$\Delta^t_{\beta-\alpha}$	$\delta^t_{\beta-\alpha}$	Reference
Paraffins								
<i>n</i> -Pentane	20	0.62624	....	1.36200	1.35587	61.3	97.9	13
2-Methylbutane	20	0.61972	....	1.35827	1.35218	60.9	98.3	13
<i>n</i> -Hexane	20	0.65943	....	1.37950	1.37300	65.0	98.6	13
2-Methylpentane	20	0.65316	....	1.37609	1.36961	64.8	99.2	13
3-Methylpentane	20	0.66435	....	1.38114	1.37470	64.4	96.9	13
2,2-Dimethylbutane	20	0.64919	....	1.37344	1.36695	64.9	99.9	13
2,3-Dimethylbutane	20	0.66166	....	1.37965	1.37313	65.2	98.5	13
<i>n</i> -Heptane	20	0.68378	....	1.39247	1.38573	67.4	98.6	13
	20	0.6836	1.3870	1.39173	1.38502	67.1	98.1	G. W.
	80	0.6323	1.3593	1.36358	1.35752	60.6	95.9	G. W.
2-Methylhexane	20	0.67869	....	1.38967	1.38292	67.5	99.5	13
2,2-Dimethylpentane	20	0.67388	....	1.38703	1.38025	67.8	100.6	13
2,3-Dimethylpentane	20	0.69514	....	1.39680	1.39007	67.3	96.8	13
2,4-Dimethylpentane	20	0.67275	....	1.38620	1.37956	66.4	98.7	13
3,3-Dimethylpentane	20	0.69330	....	1.39575	1.38901	67.4	97.2	13
2,2,3-Trimethylbutane	20	0.69007	....	1.39430	1.38751	67.9	98.4	13
<i>n</i> -Octane	20	0.70280	....	1.40252	1.39562	69.0	98.2	13
3-Methylheptane	20	0.70584	....	1.40344	1.39656	68.8	97.5	13
2,3-Dimethylhexane	20	0.71234	....	1.40617	1.39922	69.5	97.6	13
2,5-Dimethylhexane	20	0.69426	....	1.39772	1.39081	69.1	99.5	13
3,4-Dimethylhexane	20	0.71951	....	1.40924	1.40224	70.0	97.3	13
3-Methyl-3-ethylpentane	20	0.72742	....	1.41280	1.40581	69.9	96.1	13
2,2,3-Trimethylpentane	20	0.71613	....	1.40790	1.40094	69.6	97.2	13
2,2,4-Trimethylpentane	20	0.69196	....	1.39640	1.38944	69.6	100.6	13
	20	0.6918	1.3912	1.39621	1.38924	69.7	100.7	G. W.
	80	0.6404	1.3633	1.36764	1.36131	63.3	98.8	G. W.
<i>n</i> -Nonane	20	0.71808	....	1.41058	1.40353	70.5	98.2	13
<i>n</i> -Hexadecane	20	0.77387	....	1.44002	1.43242	76.0	98.2	13
Unsaturates (Straight Chain)								
2-Ethylhexene-1	20	0.7268	1.4210	1.42426	1.41544	88.2	121.4	G. W.
Diisobutene	20	0.7370	1.4122	1.4184	1.4098	86.0	116.9	G. W.
Naphthenes								
Ethylcyclobutane	20	0.72787	....	1.40719	1.40001	71.8	98.6	13
Cyclopentane	20	0.74542	....	1.41145	1.40442	70.3	94.3	13
Methylcyclopentane	20	0.74869	....	1.41488	1.40764	72.4	96.7	13
	20	0.749	1.4100	1.4153	1.4080	72.7	97.1	G. W.
Cyclohexane	20	0.77867	....	1.43157	1.42405	75.2	96.6	13
	20	0.7786	1.4254	1.43053	1.42307	74.6	95.9	G. W.
	80	0.7201	1.3953	1.40022	1.39345	67.7	93.9	G. W.
Methylcyclohexane	20	0.76944	....	1.42838	1.42085	75.3	97.9	13
	20	0.7700	1.4223	1.42754	1.42003	75.1	97.5	G. W.
	80	0.7170	1.3946	1.39961	1.39278	68.3	95.2	G. W.
Ethylcyclopentane <sup>b</sup>	20	0.7632	1.4203	1.4252	1.4179	73.0	95.6	G. W.
Isopropylcyclopentane	20	0.7764	1.4263	1.4315	1.4241	74.4	95.8	G. W.
Isopropylcyclohexane	20	0.80232	....	1.44641	1.43867	77.4	96.5	13
<i>n</i> -Butylcyclopentane	20	0.7832	1.4321	1.4375	1.4300	75.4	96.3	G. W.
Isobutylcyclopentane	20	0.7806	1.4301	1.4353	1.4278	75.5	96.7	G. W.
<i>tert</i> -Butylcyclopentane	20	0.7911	1.4341	1.4396	1.4320	76.4	96.6	G. W.
<i>sec</i> -Butylcyclopentane	20	0.7941	1.4361	1.4415	1.4339	75.7	95.4	G. W.
<i>tert</i> -Amylcyclopentane	20	0.8071	1.4457	1.4511	1.4433	78.0	96.6	G. W.
3-Cyclopentylpentane	20	0.8099	1.4443	1.4498	1.4422	76.7	94.7	G. W.
Neopentylcyclohexane	20	0.7989	1.4417	1.4473	1.4394	79.0	98.9	G. W.
Cyclohexylcyclopentane	20	0.8774	1.4726	1.4784	1.4700	83.7	95.4	G. W.
1,3-Dicyclohexylbutane	20	0.8793	1.4800	1.4860	1.4775	85.4	97.2	G. W.
Unsaturated Cyclics								
Cyclohexene	20	0.8092	1.4452	1.4520	1.4425	94.7	117.1	G. W.
Methylcyclopentene <sup>b</sup>	20	0.7791	1.4322	1.4389	1.4294	95.1	122.0	G. W.
Ethylcyclopentene	20	0.8053	1.4440	1.4507	1.4412	95.4	118.7	G. W.
<i>n</i> -Propylcyclopentene	20	0.8062	1.4461	1.4528	1.4434	94.3	117.0	G. W.
<i>n</i> -Butylcyclopentene	20	0.8138	1.4496	1.4562	1.4468	93.7	115.2	G. W.
<i>tert</i> -Butylcyclopentene	20	0.8021	1.4421	1.4486	1.4397	88.8	110.7	G. W.
<i>tert</i> -Amylcyclopentene	20	0.8256	1.4554	1.4618	1.4527	90.8	110.0	G. W.
4- <i>tert</i> -Butylcyclohexene	20	0.8315	1.4602	1.4667	1.4575	91.6	110.2	G. W.
4- <i>tert</i> -Amylcyclohexene	20	0.841	1.4676	1.4740	1.4649	91.3	108.5	G. W.
Aromatics								
Benzene	20	0.8789	1.5011	1.51318	1.49646	167.2	190.2	G. W.
	80	0.8135	1.4640	1.47505	1.45982	152.3	187.2	G. W.
Toluene	20	0.8669	1.4964	1.50781	1.49178	160.3	184.9	G. W.
	80	0.8097	1.4647	1.47539	1.46062	147.7	182.4	G. W.
Ethylbenzene	20	0.8681	1.4957	1.50668	1.49151	151.7	174.7	G. W.
<i>o</i> -Xylene	20	0.8796	1.5046	1.51594	1.50013	158.1	179.7	G. W.
<i>m</i> -Xylene	20	0.8647	1.4973	1.50869	1.49301	156.8	181.3	G. W.
<i>p</i> -Xylene	20	0.8616	1.4957	1.50709	1.49141	156.8	181.9	G. W.

<sup>a</sup> For lack of a definite value for the temperature coefficient some of the authors' own values (G. W.) are reported to the fourth decimal place only.  
<sup>b</sup> The cyclopentanes and -pentenes used were synthesized by H. Pines of the Universal Oil laboratories, and the authors gratefully acknowledge the loan of these hydrocarbons.

dispersion of  $99 \pm 1$ . The specific dispersions of aromatics and olefins are substantially higher, as illustrated in Figure 1, which is based on data compiled by Fuchs and Anderson (3), Ward and Kurtz (11), and the authors' own determinations. The latter are given in Table I, together with recent measurements of Wibaut, Smittenberg, and co-workers (13).  
In first approximation, the specific dispersion increments due to aromatics or olefins are straight-line functions of their concentration. For aromatics this is shown in Figure 2. Line 1 shows the specific dispersion of benzene in mixtures with *n*-heptane and cyclohexane and line 2 shows toluene in mixtures with 2,2,4-trimethylpentane and methylcyclohexane. The experimental points are drawn in and indicate the deviation. Measurements on these two series were made with a Pulfrich refractometer. Whereas these two mixtures represent close-boiling mixtures, which can be expected to be

TABLE II. MIXTURES OF *n*-PENTANE AND 1-METHYLNAPHTHALENE

	No. 74	No. 74-A	No. 74-B	No. 74-C	No. 74-D
Weight % 1-Methylnaphthalene	0	33.40	61.57	82.80	100
<i>n</i> -Pentane	100	66.60	38.43	17.20	0
$d_4^{20}$	0.6259	0.7270	0.8338	0.9308	1.0201
$n_D^{20}$	1.3576	1.4222	1.4920	1.5564	1.6170
$Z$	41.8	38.4	34.4	30.0	24.3
$\Delta$ (Abbé)	64.7	118.0	181.2	243.1	303.1
$\delta$ (Abbé)	103.4	162	217	261	297

typical of mixtures obtained in practical fractionations, curve 3 represents an extreme case of liquids with widely differing boiling ranges and densities—namely, 1-methylnaphthalene (boiling point 243° C.,  $d_4^{20} = 1.0201$ ) and *n*-pentane (boiling point 36.08° C.,  $d_4^{20} = 0.6261$ )—based on data given in Table II. Even in this case the deviation from linearity is not large.



For olefins the effect of concentration on specific dispersion is shown in Figure 3; here the specific dispersion of a mixture of 2-ethylhexene-1 with saturated hydrocarbons is plotted against the experimental bromine number.

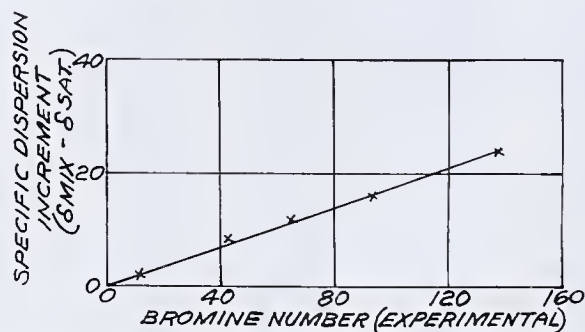


FIGURE 3. EFFECT OF OLEFIN (2-ETHYLHEXENE-1, BROMINE No. 138) IN RAISING SPECIFIC DISPERSION OF SATURATES

It is a very important fact that this relationship<sup>2</sup> between increase in specific dispersion and the concentration of the double bond is general and holds good within reasonable accuracy, regardless of whether this concentration is changed by mixing an olefin with saturated hydrocarbons or whether the change is produced in the molecule of the olefin itself by changing the number of carbon atoms. It is true, therefore, also for diolefins, as well as for cyclic mono- and diolefins. This is illustrated in Figure 4, based on data of Tables I and XI.

The only exceptions are the conjugated diolefins. Conjugation produces abnormally high specific dispersions. Mixtures likely to contain them must be tested, and if present, they have to be eliminated by means of the Diels-Alder reaction as described below.

Any accurate method for determining unsaturation, such as bromine, iodine, or hydrogen number, etc., permits one to calculate the specific dispersion increment contributed by the double bonds. (Any inherent error in the determination of unsaturation will, of course, enter also into the method and should be guarded against. It is recommended that the bromine number, as well as the dispersion, of a known aromatic-free sample always be determined as a check.)

When bromine numbers are used to determine the unsaturation the following formula may be used:

$$\delta_{\text{olefins}} - \delta_{\text{saturates}} = \Delta \delta_{\text{olefins}} = 0.16 \times \text{bromine number}$$

For example, in a hydrocarbon mixture of bromine number 10, the increment due to olefins will be 1.6 specific dispersion units.

The specific dispersion of a mixture of paraffinic, naphthenic, aromatic, and olefinic hydrocarbons boiling in the gasoline range can be expressed within reasonable accuracy by the equation

$$\delta_{\text{mixt.}} = \delta_{\text{sats.}} + \frac{(\delta_{\text{arom.}} - \delta_{\text{sats.}}) \times \text{weight \% of aromatics}}{100} + \frac{(\delta_{\text{olefins}} - \delta_{\text{sats.}}) \times \text{weight \% of olefins}}{100}$$

where  $\delta_{\text{arom.}}$  and  $\delta_{\text{olefins}}$  are the average specific dispersions of the pure aromatics and pure olefins present in the mixture.

Since the values of the specific dispersion of the saturates are practically always  $99 \pm 1$  and the contribution due to olefins is equal to  $0.16 \times \text{bromine number}$ , the weight per cent of aromatics in the mixture will be given by the equation

weight % of aromatics =

$$\frac{\delta_{\text{mixt.}} - 0.16 \times \text{bromine number} - 99}{\delta_{\text{arom.}} - 99} \times 100$$

The values of the specific dispersion for aromatics boiling in various selected cuts of the gasoline range are as follows:

° C.		
70-95	Benzene	190.2
95-122	Toluene	184.9
122-150	Xylenes and ethylbenzene	179.2
150-175	C <sub>9</sub> and C <sub>10</sub> aromatics (av.)	175.0
175-200	C <sub>10</sub> and C <sub>11</sub> aromatics (av.)	171.0

Thole (7) and Tizard and Marshall (8) have studied the separation by fractionation of the lower boiling aromatics and recommended the cutting temperatures of  $95^\circ$ —i. e.,  $70^\circ$  to  $95^\circ$ —and  $122^\circ$  C.—i. e.,  $95^\circ$  to  $122^\circ$ . For most cases, however, the dispersion method will give results within the experimental error if the usual cutting temperatures of  $100^\circ$  C.—i. e.,  $70^\circ$  to  $100^\circ$ —and  $125^\circ$  C.—i. e.,  $100^\circ$  to  $125^\circ$ —are used. The analyst should select the correct temperatures after giving consideration to the efficiency of the fractionation column and to further type analysis, such as determination of C<sub>6</sub>, C<sub>7</sub>, C<sub>8</sub>, and C<sub>9</sub> paraffins.

For such cuts, therefore, the weight per cent of aromatics may readily be calculated using the above equation, or more accurately by means of Table III, which takes into consideration any deviations from the straight-line relationship. For wider boiling cuts, values averaged from the above may be used.

### Measurement of Dispersion

The dispersion of a liquid sample may be determined in the course of 0.5 to 1 minute on a standard Abbé refractometer simultaneously with the  $n_D$  determination. Daylight is used and the dispersion angle,  $Z$ , is read off the ring at the lower end of the tube (A, Figure 5) and converted to dispersion for the  $H_\beta - H_\alpha$  lines by means of an equation supplied with each instrument. The procedure for taking readings recommended by the firm of C. Zeiss or the Bausch & Lomb Optical Company should be strictly adhered to.

The dispersions obtained on the Abbé refractometer vary within  $\pm 1$  to 2 units if measured by an experienced observer. For accurate measurements the Pulfrich refractometer of C. Zeiss Co., Jena, is recommended. With this instrument the index of refraction may be measured for any desired wave length in the visible spectrum. Using a hydrogen-filled Geissler tube the  $n_{H_\beta} - n_{H_\alpha}$  dispersion can be determined with an accuracy of  $\pm 0.1$  to 0.2 unit. Since the dispersion is measured by difference (micrometric screw) it is more accurate than the absolute values of the indices.

After the density (Westphal balance, areometer, or pycnometer) and bromine number of the fraction are known, the aromatic content can be determined in a minute or two. Table III is used to convert the specific dispersion of the mixture, corrected for any olefinic content, directly into weight per cent of aromatics; in preparing this table consideration was given to the straight-line deviations.

The Abbé dispersion angles or  $Z$  values have to be converted into dispersions by means of the equation

$$\Delta_{H_\beta - H_\alpha} = n^F - n^C = (A + B_\sigma) \times 10,000$$

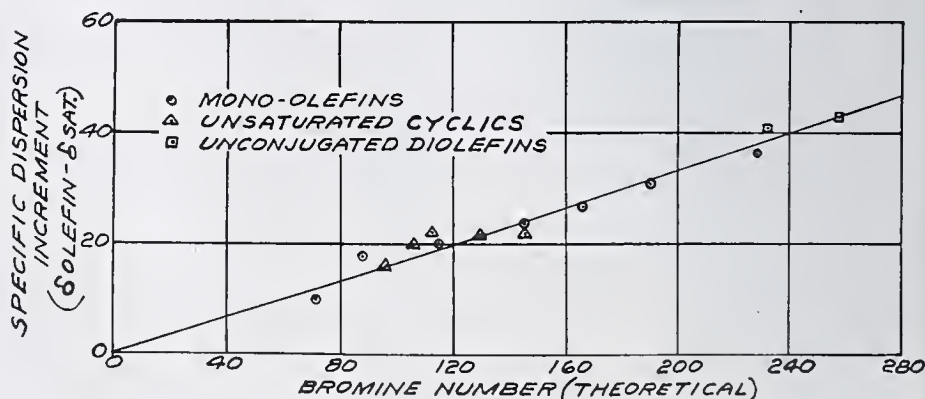


FIGURE 4. SPECIFIC DISPERSION VS. BROMINE NUMBER FOR UNSATURATES



TABLE III. SPECIFIC DISPERSION,  $\delta_{H\beta} - H_{\alpha}$ , OF GASOLINE AND NAPHTHA CUTS

(Corrected to olefin-free basis)											
Weight % of Aromatics	Benzene	Toluene	Xylenes and Ethyl- benzene	C <sub>3</sub> and C <sub>4</sub> Alkyl- benzenes	C <sub>4</sub> and C <sub>5</sub> Alkyl- benzenes	Weight % of Aromatics	Benzene	Toluene	Xylenes and Ethyl- benzene	C <sub>3</sub> and C <sub>4</sub> Alkyl- benzenes	C <sub>4</sub> and C <sub>5</sub> Alkyl- benzenes
	Cutting Temperatures						Cutting Temperatures				
	70-95° or 70-100° C.	95-122° or 100-125° C.	122-150° or 125-150° C.	150-175° C.	175-200° C.		70-95° or 70-100° C.	95-122° or 100-125° C.	122-150° or 125-150° C.	150-175° C.	175-200° C.
0	98.0	99.0	99.0	99.0	99.0	51	143.1	141.6	139.4	137.8	135.7
1	98.9	99.8	99.8	99.8	99.7	52	144.0	142.4	140.2	138.5	136.4
2	99.7	100.6	100.6	100.5	100.4	53	145.0	143.3	141.0	139.3	137.2
3	100.6	101.4	101.3	101.3	101.2	54	145.9	144.1	141.8	140.0	137.9
4	101.4	102.2	102.1	102.0	101.9	55	146.8	145.0	142.7	140.8	138.6
5	102.3	103.0	102.9	102.8	102.6	56	147.8	145.9	143.5	141.6	139.3
6	103.1	103.9	103.7	103.6	103.3	57	148.7	146.7	144.3	142.3	140.0
7	104.0	104.7	104.5	104.3	104.0	58	149.6	147.6	145.1	143.1	140.8
8	104.8	105.5	105.2	105.1	104.8	59	150.5	148.4	145.9	143.8	141.5
9	105.7	106.3	106.0	105.8	105.5	60	151.5	149.3	146.7	144.6	142.2
10	106.5	107.1	106.8	106.6	106.2	61	152.4	150.2	147.5	145.4	142.9
11	107.4	107.9	107.6	107.4	106.9	62	153.4	151.1	148.3	146.1	143.6
12	108.2	108.8	108.4	108.1	107.6	63	154.3	151.9	149.1	146.9	144.4
13	109.1	109.6	109.2	108.9	108.4	64	155.3	152.8	149.9	147.6	145.1
14	110.0	110.4	110.0	109.6	109.1	65	156.2	153.7	150.7	148.4	145.8
15	110.8	111.3	110.8	110.4	109.8	66	157.2	154.6	151.5	149.2	146.5
16	111.7	112.1	111.5	111.2	110.5	67	158.1	155.5	152.3	149.9	147.2
17	112.6	112.9	112.3	111.9	111.2	68	159.1	156.3	153.1	150.7	148.0
18	113.4	113.8	113.1	112.7	112.0	69	160.0	157.2	153.9	151.4	148.7
19	114.3	114.6	113.9	113.4	112.7	70	160.9	158.1	154.7	152.2	149.4
20	115.2	115.4	114.7	114.2	113.4	71	161.9	159.0	155.5	153.0	150.1
21	116.0	116.2	115.5	115.0	114.1	72	162.8	159.9	156.3	153.7	150.8
22	116.9	117.1	116.3	115.7	114.8	73	163.8	160.7	157.1	154.5	151.6
23	117.8	117.9	117.1	116.5	115.6	74	164.7	161.6	157.9	155.2	152.3
24	118.7	118.7	117.9	117.2	116.3	75	165.7	162.5	158.8	156.0	153.0
25	119.6	119.6	118.7	118.0	117.0	76	166.7	163.4	159.6	156.8	153.7
26	120.5	120.4	119.4	118.8	117.7	77	167.6	164.3	160.4	157.5	154.5
27	121.4	121.2	120.2	119.5	118.4	78	168.6	165.1	161.2	158.3	155.2
28	122.3	122.1	121.0	120.3	119.2	79	169.5	166.0	162.0	159.2	155.9
29	123.2	122.9	121.8	121.0	119.9	80	170.5	166.9	162.8	159.8	156.6
30	124.1	123.7	122.6	121.8	120.6	81	171.5	167.8	163.6	160.6	157.3
31	125.0	124.5	123.4	122.6	121.3	82	172.4	168.7	164.4	161.3	158.0
32	125.9	125.4	124.2	123.3	122.0	83	173.4	169.6	165.3	162.1	158.8
33	126.8	126.2	125.0	124.1	122.8	84	174.4	170.5	166.1	162.8	159.5
34	127.7	127.1	125.8	124.8	123.5	85	175.4	171.4	166.9	163.6	160.2
35	128.6	127.9	126.6	125.6	124.2	86	176.3	172.2	167.7	164.4	160.9
36	129.5	128.7	127.4	126.4	124.9	87	177.3	173.1	168.5	165.1	161.6
37	130.4	129.6	128.2	127.1	125.6	88	178.3	174.0	169.3	165.9	162.4
38	131.3	130.4	129.0	127.9	126.4	89	179.2	174.9	170.2	166.6	163.1
39	132.2	131.3	129.8	128.6	127.1	90	180.2	175.8	171.0	167.4	163.8
40	133.1	132.1	130.6	129.4	127.8	91	181.2	176.7	171.8	168.2	164.5
41	134.0	133.0	131.4	130.2	128.5	92	182.2	177.6	172.6	168.9	165.2
42	134.9	133.8	132.2	130.9	129.2	93	183.2	178.5	173.5	169.7	166.0
43	135.8	134.7	133.0	131.7	130.0	94	184.2	179.4	174.3	170.4	166.7
44	136.7	135.5	133.8	132.4	130.7	95	185.2	180.4	175.1	171.2	167.4
45	137.6	136.4	134.6	133.2	131.4	96	186.2	181.3	175.9	172.0	168.1
46	138.5	137.3	135.4	134.0	132.1	97	187.1	182.2	176.7	172.7	168.8
47	139.4	138.1	136.2	134.7	132.8	98	188.1	183.1	177.6	173.5	169.6
48	140.3	139.0	137.0	135.5	133.6	99	189.1	184.0	178.4	174.2	170.3
49	141.2	139.8	137.8	136.2	134.3	100	190.1	184.9	179.2	175.0	171.0
50	142.2	140.7	138.6	137.0	135.0						

Corrections to Be Added to Experimental Specific Dispersions of Mixtures with Change in Base Value of Saturated Hydrocarbon Mixture

Weight % of Aromatics	Base Value for Saturates					Weight % of Aromatics	Base Value for Saturates				
	96.0	97.0	98.0	99.0	100.0		96.0	97.0	98.0	99.0	100.0
	Benzene						Toluene and Higher				
0	+2.0	+1.0	0	-1.0	-2.0	0	+3.0	+2.0	+1.0	0	-1.0
10	+1.8	+0.9	0	-0.9	-1.8	10	+2.7	+1.8	+0.9	0	-0.9
20	+1.6	+0.8	0	-0.8	-1.6	20	+2.4	+1.6	+0.8	0	-0.8
30	+1.4	+0.7	0	-0.7	-1.4	30	+2.1	+1.4	+0.7	0	-0.7
40	+1.2	+0.6	0	-0.6	-1.2	40	+1.8	+1.2	+0.6	0	-0.6
50	+1.0	+0.5	0	-0.5	-1.0	50	+1.5	+1.0	+0.5	0	-0.5
60	+0.8	+0.4	0	-0.4	-0.8	60	+1.2	+0.8	+0.4	0	-0.4
70	+0.6	+0.3	0	-0.3	-0.6	70	+0.9	+0.6	+0.3	0	-0.3
80	+0.4	+0.2	0	-0.2	-0.4	80	+0.6	+0.4	+0.2	0	-0.2
90	+0.2	+0.1	0	-0.1	-0.2	90	+0.3	+0.2	+0.1	0	-0.1
100	0.0	0.0	0	0.0	0.0	100	0.0	0.0	0.0	0	0.0

where  $A$  and  $B$  are constants depending on the  $n_D$  and dispersion of the particular batch of glass used in the preparation of the refractometer's prism and  $\sigma$  is a function of  $Z$ .

Each Abbé refractometer is supplied with a table giving the values for these quantities; furthermore, the number of the dispersion table to be used with a particular instrument is always stamped in the lower right-hand corner of the index scale.

In order to convert the angle reading directly and immediately into dispersions, Table IV has been prepared. It takes the place of C. Zeiss dispersion table No. 30, and may be used for every refractometer having the number 30 on the lower right-hand corner of the index scale. Tables similar to Table IV can be calculated for any given pair of the  $A$  and  $B$  constants.

### Results with Synthetic Mixtures

A number of synthetic mixtures containing varying amounts of aromatics, paraffins, naphthenes, and olefins were

prepared and their  $n_D$ ,  $n_{H\beta}$ ,  $n_{H\alpha}$ ,  $d_4^{20}$ ,  $\Delta$ ,  $\delta$ , and bromine numbers (Francis' method) determined. Benzene, toluene, and a mixture of xylenes and ethylbenzene were taken as representative of aromatics. *n*-Heptane and 2,2,4-trimethylpentane, and cyclohexane and methylcyclohexane were chosen as representatives of the paraffins and naphthenes, respectively. The unsaturates used were 2-ethylhexene-1, 2-methylbutadiene-1,3 (isoprene), and 2-methylpentadiene-1,3. The properties of the pure hydrocarbons, as used by the authors, are given in Table I. All data, including both the Abbé (Zeiss No. 49,242) and Pulfrich refractometer (Zeiss No. N-59,956) measurements, are correlated in Tables V to IX. As can be seen, the accuracy of measurement with the Abbé instrument is sufficient for many practical purposes, such as control analysis. However, for more accurate analysis the Pulfrich instrument gives results to approximately  $\pm 1$  per cent of the aromatic content.



TABLE IV. DISPERSIONS,

(As a function of Z and  $n_D$ , in Z range 10 to 50 and

Z <sub>m</sub>	1.350	1.360	1.370	1.380	1.390	1.400	1.410	1.420	1.430	1.440	1.450	1.460	1.470	1.480	1.490
10	522.3	520.1	517.8	515.3	512.7	509.8	507.0	504.0	501.0	497.7	494.5	491.0	487.4	483.7	479.9
11	513.8	511.6	509.4	506.9	504.4	501.6	498.9	496.0	493.0	489.8	486.7	483.3	479.8	476.3	472.5
12	504.3	501.8	499.7	497.3	494.8	492.5	489.5	486.7	483.8	480.8	478.0	474.7	471.4	467.9	464.3
13	494.1	492.7	490.0	487.7	485.3	482.7	480.2	477.4	474.6	471.7	468.8	465.6	462.4	459.1	455.6
14	483.3	481.4	479.3	477.2	474.8	472.3	469.9	467.3	464.6	461.8	459.0	455.9	452.8	449.6	446.3
15	471.9	470.0	468.1	466.0	463.7	461.4	459.0	456.5	453.9	451.2	448.6	445.6	442.7	439.7	436.5
16	459.9	458.1	456.2	454.2	452.1	449.8	447.5	445.1	442.7	440.1	437.6	434.8	432.0	429.1	426.1
17	447.2	445.5	443.7	441.8	439.7	437.6	435.5	433.2	430.9	428.4	426.0	423.4	420.7	418.0	415.2
18	434.2	432.6	430.9	429.1	427.1	425.1	423.1	420.9	418.7	416.4	414.2	411.7	409.2	406.7	404.0
19	420.6	419.0	417.4	415.7	413.9	412.0	410.1	408.1	406.0	403.9	401.8	399.4	397.1	394.7	392.2
20	406.3	404.9	403.4	401.8	400.1	398.3	396.5	394.6	392.7	390.7	388.8	386.6	384.5	382.3	380.0
21	391.7	390.4	389.0	387.5	385.9	384.2	382.6	380.8	379.1	377.2	375.5	373.5	371.5	369.5	367.4
22	376.8	375.6	374.3	372.9	371.4	369.9	368.4	366.8	365.2	363.5	361.9	360.1	358.3	356.5	354.6
23	361.3	360.1	358.9	357.7	356.4	355.0	353.6	352.1	350.7	349.2	347.7	346.1	344.5	342.9	341.2
24	345.8	344.7	343.6	342.5	341.3	340.0	338.8	337.5	336.2	334.9	333.6	332.1	330.7	329.3	327.8
25	329.9	329.0	328.0	327.0	325.9	324.8	323.7	322.5	321.4	320.2	319.1	317.9	316.7	315.4	314.1
26	313.7	312.9	312.0	311.1	310.2	309.2	308.3	307.3	306.3	305.3	304.4	303.3	302.3	301.3	300.2
27	297.3	296.5	295.8	295.0	294.2	293.4	292.6	291.7	290.9	290.1	289.4	288.5	287.7	286.9	286.0
28	280.8	280.1	279.5	278.9	278.2	277.5	276.9	276.2	275.6	274.9	274.3	273.7	273.1	272.4	271.8
29	264.3	263.8	263.3	262.7	262.2	261.7	261.2	260.6	260.2	259.7	259.3	258.8	258.4	258.0	257.6
30	247.8	247.4	247.0	246.6	246.2	245.8	245.5	245.1	244.8	244.5	244.3	244.0	243.8	243.6	243.4
31	231.3	231.0	230.7	230.5	230.2	229.9	229.8	229.6	229.4	229.3	229.3	229.2	229.2	229.2	229.2
32	214.8	214.7	214.5	214.3	214.2	214.1	214.1	214.0	214.0	214.1	214.3	214.3	214.3	214.8	215.0
33	198.3	198.3	198.2	198.2	198.2	198.2	198.4	198.5	198.7	198.9	199.2	199.5	199.8	200.3	200.8
34	181.9	181.9	182.0	182.1	182.2	182.4	182.7	182.9	183.3	183.7	184.2	184.7	185.3	185.9	186.6
35	165.7	165.8	166.0	166.2	166.5	166.8	167.3	167.7	168.2	168.8	169.5	170.1	170.9	171.8	172.7
36	149.8	150.1	150.4	150.7	151.1	151.6	152.2	152.7	153.4	154.1	155.0	155.9	156.9	157.8	159.0
37	134.3	134.7	135.1	135.5	136.0	136.6	137.4	138.1	138.9	139.8	140.9	141.9	143.1	144.3	145.6
38	118.8	119.2	119.7	120.3	121.0	121.7	122.6	123.4	124.4	125.5	126.7	127.9	129.3	130.7	132.2
39	103.9	104.4	105.0	105.7	106.5	107.4	108.4	109.4	110.5	111.8	113.1	114.5	116.1	117.7	119.4
40	89.3	89.9	90.6	91.4	92.3	93.3	94.5	95.6	96.9	98.3	99.8	101.4	103.1	104.9	106.8
41	75.0	75.8	76.6	77.5	78.5	79.6	80.9	82.1	83.6	85.1	86.8	88.6	90.5	92.5	94.6
42	61.4	62.2	63.1	64.1	65.3	66.5	67.9	69.3	70.9	72.6	74.4	76.3	78.4	80.5	82.8
43	48.4	49.3	50.3	51.4	52.7	54.0	55.5	57.0	58.7	60.6	62.6	64.6	66.9	69.2	71.6
44	35.7	36.7	37.8	39.0	40.3	41.8	43.5	45.1	46.9	48.9	51.0	53.2	55.6	58.1	60.7
45	23.7	24.8	25.9	27.2	28.7	30.2	32.0	33.7	35.7	37.8	40.0	42.4	44.9	47.5	50.3
46	12.3	13.4	14.7	16.0	17.6	19.3	21.1	22.9	25.0	27.2	29.6	32.1	34.8	37.6	40.5
47	1.5	2.7	4.0	5.5	7.1	8.9	10.8	12.8	15.0	17.3	19.8	22.4	25.2	28.1	31.2
48	...	...	...	...	...	...	1.5	3.5	5.8	8.2	10.6	13.3	16.2	19.3	22.5
49	...	...	...	...	...	...	...	...	...	...	1.9	4.7	7.8	10.9	14.3
50	...	...	...	...	...	...	...	...	...	...	...	...	0.2	3.5	6.9

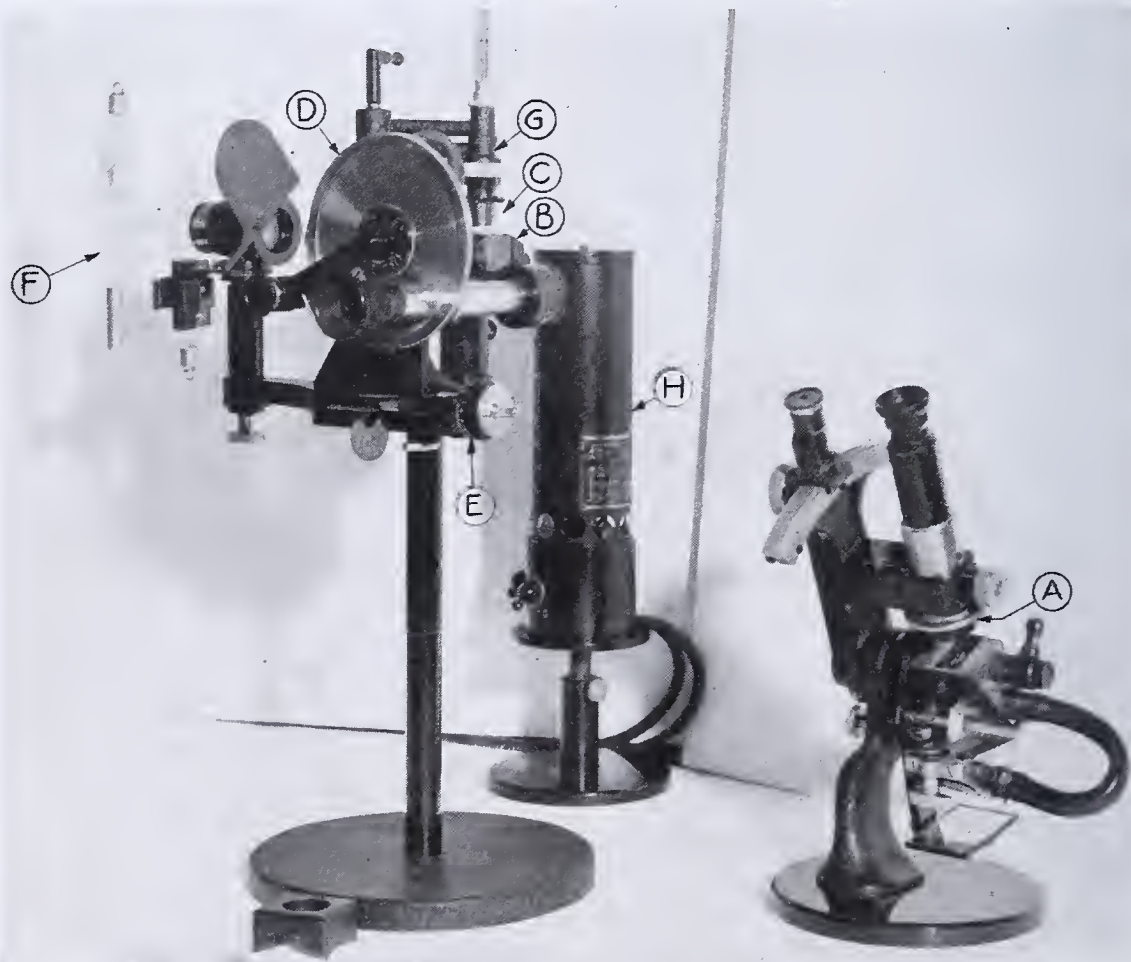


FIGURE 5. PULFRICH (left) AND ABBÉ (right) REFRACTOMETERS

- A. Dispersion angle (Z) ring
- B. Prism
- C. Glass ring for sample
- D. Graduated circle for measuring angle of light
- E. Micrometric screw
- F. Geissler tube
- G. Constant-temperature device
- H. Sodium lamp for measuring  $n_D$



Δ<sub>β-α</sub>, i. e. (n<sub>Hβ</sub> - n<sub>Hα</sub>) · 10,000  
n<sub>D</sub> 1.350 to 1.650. For C. Zeiss Dispersion Table 30)

Z <sub>30</sub>	1.500	1.510	1.520	1.530	1.540	1.550	1.560	1.570	1.580	1.590	1.600	1.610	1.620	1.630	1.640	1.650
10	476.0	471.9	467.8	463.3	458.8	454.1	449.3	444.3	439.0	433.6	427.9	422.0	415.9	409.7	403.2	396.5
11	468.7	464.8	460.8	456.5	452.1	447.6	442.9	438.0	432.9	427.7	422.2	416.5	410.6	404.5	398.3	391.8
12	460.7	456.9	453.0	448.8	444.6	440.3	435.7	430.8	425.9	420.9	415.8	410.1	404.4	398.6	392.8	386.4
13	452.1	448.4	444.7	440.7	436.7	432.5	428.1	423.6	418.9	414.1	409.0	403.8	398.3	392.7	387.0	381.0
14	442.9	439.4	435.9	432.0	428.2	424.2	420.0	415.7	411.2	406.6	401.7	396.8	391.6	386.2	380.8	375.1
15	432.3	429.9	426.5	422.9	419.2	415.4	411.4	407.4	403.1	398.7	394.1	389.4	384.4	379.4	374.2	368.8
16	423.1	419.9	416.7	413.2	409.7	406.1	402.4	398.5	394.5	390.3	386.0	381.5	376.9	372.1	367.3	362.2
17	412.3	409.3	406.3	403.1	399.8	396.4	392.9	389.3	385.5	381.6	377.5	373.3	369.0	364.5	360.0	355.2
18	401.3	398.5	395.7	392.6	289.6	386.4	383.1	379.7	376.2	372.6	368.7	364.9	360.8	356.7	352.5	348.1
19	389.7	387.1	384.5	381.7	378.9	375.9	372.9	369.7	366.5	363.1	359.6	356.1	352.3	348.5	344.7	340.6
20	377.7	375.3	372.9	370.3	367.7	365.0	362.2	359.3	356.3	353.3	350.1	346.8	343.4	340.0	336.5	332.8
21	365.3	363.1	360.9	358.6	356.2	353.7	351.2	348.6	345.9	343.2	340.3	337.3	334.3	331.2	328.1	324.7
22	352.7	350.7	348.7	346.6	344.5	342.3	340.0	337.7	335.3	332.8	330.3	327.7	325.0	322.2	319.5	316.6
23	339.5	337.7	336.0	334.1	332.3	330.3	328.3	326.3	324.2	322.1	319.8	317.6	315.3	312.9	310.5	308.0
24	326.3	324.8	323.3	321.7	320.1	318.4	316.7	314.9	313.1	311.3	309.4	307.5	305.5	303.6	301.6	299.5
25	312.9	311.6	310.4	309.0	307.6	306.2	304.8	303.3	301.8	300.4	298.8	297.3	295.6	294.0	292.5	290.8
26	299.2	298.1	297.1	296.0	294.9	293.8	292.6	291.5	290.3	289.2	287.9	286.8	285.5	284.3	283.2	281.9
27	285.2	284.4	283.7	282.8	282.0	281.1	280.2	279.4	278.6	277.7	276.9	276.1	275.2	274.4	273.7	272.9
28	271.2	270.7	270.2	269.5	269.0	268.4	267.9	267.3	266.8	266.3	265.8	265.4	264.9	264.5	264.2	263.8
29	257.3	256.9	256.7	256.3	256.1	255.8	255.5	255.3	255.1	254.9	254.8	254.7	254.6	254.6	254.7	254.8
30	243.3	243.2	243.2	243.1	243.1	243.1	243.1	243.2	243.3	243.5	243.7	244.0	244.3	244.7	245.2	245.7
31	229.3	229.5	229.7	229.9	230.1	230.4	230.7	231.1	231.5	232.1	232.6	233.3	234.0	234.8	235.7	236.6
32	215.4	215.7	216.2	216.7	217.2	217.8	218.3	219.1	219.8	220.7	221.6	222.6	223.7	224.9	226.2	227.6
33	201.4	202.0	202.7	203.4	204.2	205.1	206.0	207.0	208.0	209.3	210.5	211.9	213.4	215.0	216.7	218.5
34	187.4	188.3	189.3	190.2	191.3	192.4	193.6	194.9	196.3	197.8	199.5	201.2	203.1	205.1	207.2	209.5
35	173.7	174.8	176.0	177.2	178.6	180.0	181.4	183.1	184.8	186.6	188.6	190.7	193.0	195.4	197.9	200.6
36	160.3	161.6	163.1	164.5	166.1	167.8	169.5	171.5	173.5	175.7	178.0	180.5	183.1	185.8	188.8	191.9
37	147.1	148.7	150.4	152.1	153.9	155.9	157.9	160.1	162.4	164.9	167.6	170.4	173.3	176.5	179.9	183.4
38	133.9	135.7	137.7	139.6	141.7	143.9	146.2	148.7	151.3	154.2	157.1	160.3	163.6	167.2	170.9	174.8
39	121.3	123.3	125.5	127.6	130.0	132.5	135.0	137.8	140.7	143.8	147.1	150.7	154.3	158.2	162.3	166.7
40	108.9	111.1	113.5	115.9	118.5	121.2	124.0	127.1	130.3	133.7	137.3	141.2	145.2	149.4	153.9	158.6
41	96.9	99.3	101.9	104.5	107.3	110.3	113.3	116.7	120.1	123.9	127.8	131.1	136.3	140.9	145.7	150.8
42	85.3	87.9	90.7	93.6	96.6	99.8	103.1	106.7	110.4	114.4	118.7	123.1	127.8	132.7	137.9	143.3
43	74.3	77.1	80.1	83.1	86.4	89.8	93.3	97.1	101.1	105.4	109.9	114.7	119.6	124.9	130.4	136.2
44	63.5	66.5	69.7	73.0	76.5	80.1	83.8	87.9	92.1	96.7	101.4	106.5	111.7	117.3	123.1	129.2
45	54.3	56.5	59.9	63.3	67.0	70.8	74.8	79.0	83.5	88.3	93.3	98.6	104.2	110.0	116.2	122.6
46	43.7	47.0	50.5	54.2	58.0	62.0	66.2	70.7	75.4	80.4	85.7	91.2	97.0	103.2	109.6	116.3
47	34.5	38.0	41.7	45.5	49.5	53.7	58.1	62.8	67.7	72.9	78.4	84.2	90.3	96.7	103.4	110.4
48	25.9	29.5	33.4	37.4	41.6	45.9	50.5	55.6	60.7	66.1	71.6	77.9	84.2	90.8	97.6	105.0
49	17.9	21.6	25.6	29.7	34.1	38.6	43.3	48.4	53.7	59.3	65.2	71.5	78.0	84.9	92.1	99.6
50	10.6	14.5	18.6	22.9	27.4	32.1	36.9	42.1	47.6	53.4	59.5	66.0	72.7	79.7	87.2	94.9

TABLE V. BENZENE SERIES (NO OLEFINS)

	No. 126	No. 66-A	No. 66-B	No. 66-C	No. 118-A	No. 119-A	No. 66-D
Weight % Benzene	0	11.89	30.21	53.73	54.11	52.22	78.69
n-Heptane	48.44	41.11	32.52	21.77	0	47.78	9.80
Cyclohexane	51.56	47.00	37.27	24.50	45.89	0	11.51
d <sub>4</sub> <sup>20</sup>	0.7270	0.7423	0.7650	0.7978	0.8244	0.7696	0.8391
By Abbé							
Z	.....	40.9	40.0	38.7	.....	.....	37.1
n <sub>D</sub> <sup>20</sup>	.....	1.4143	1.4284	1.4493	.....	.....	1.4754
Δ	.....	82.9	96.6	117.1	.....	.....	142.4
δ	.....	112	126	147	.....	.....	170
Benzene, % (from Table III)	.....	16	32	55	.....	.....	80
Deviation	.....	+4.1	+1.8	+1.3	.....	.....	+1.3
By Pulfrich							
n <sub>D</sub> <sup>20</sup>	1.4050	1.4142	1.4282	1.4493	1.4611	1.4365	1.4751
Δ	70.4	79.5	94.6	116.1	120.0	110.4	141.4
δ	96.8	107.1	123.7	145.5	145.5	143.4	168.5
Benzene, % (from Table III and corrections)	0	11.8	30.4	54.1	54.1	51.9	78.3
Deviation	0.0	-0.1	+0.2	+0.4	0.0	-0.3	-0.4

Straight-Line Deviations of Specific Dispersion vs. Concentration Relation

The deviation from a straight-line function of the specific dispersion vs. concentration relation in the benzene, toluene, and xylene series appears only when precision Pulfrich refractometer measurements are made. The Pulfrich experimental data were found to fit equations of the type:

δ = A + BW + CW<sup>2</sup>

where W represents the weight per cent of aromatics. The following equations were obtained by the least square method from the data of Tables I, V, and VI.

- 70° to 100° C. (benzene): δ = 96.9 + 0.8577W + 0.000744W<sup>2</sup> (1)
- 100° to 125° C. (toluene): δ = 99.1 + 0.8076W + 0.000504W<sup>2</sup> (2)
- 125° to 150° C. (xylenes and ethylbenzene): δ = 99.1 + 0.7822W + 0.000188W<sup>2</sup> (3)

The average (±) deviations in weight per cent of aromatics are in the first two cases 0.2 and 0.1, respectively, and actual deviations are shown in the tables.

Comparison of the above equations shows that as the boiling range increases the equation approaches more closely a straight-line function.

The deviation of the specific dispersion from a straight line at the 50 per cent point is in each case 1.9, 1.3, and 0.5 unit, respectively. This rapid decrease indicates that as the number of side chains in the aromatic hydrocarbon increases—i. e., as its “paraffinicity” increases—more ideal solutions are produced. It seemed reasonable, therefore, to assume a straight-line relationship of δ and W in the boiling ranges 150° to 175° and 175° to 200° C. The equations covering these ranges are as follows:

- 150° to 175° C.: δ = 99 + 0.76W (4)
- 175° to 200° C.: δ = 99 + 0.72W (5)

The base value of 99 for paraffins and naphthenes is reasonable in view of existing literature data. The lower value (96.9) in Equation 1 is due to the fact that both cyclohexane and n-heptane as used in these mixtures have specific dispersions slightly lower than 99. In typical gasoline analysis a



TABLE VI. TOLUENE SERIES (NO OLEFINS)

	No. 127	No. 68-A	No. 68-B	No. 68-C	No. 68-D	No. 144 (Xylenes)
Weight %						
Toluene	0	12.05	27.01	54.77	77.71	0
<i>o</i> -Xylene	0	0	0	0	0	10.59
<i>m</i> -Xylene	0	0	0	0	0	12.18
<i>p</i> -Xylene	0	0	0	0	0	13.16
Ethylbenzene	0	0	0	0	0	13.98
2,2,4-Trimethylpentane	49.65	42.51	34.33	21.17	10.59	24.87
Methylcyclohexane	50.35	45.44	38.66	24.06	11.70	25.22
$d_4^{20}$	0.7294	0.7434	0.7606	0.7983	0.8305	0.7915
By Abbé						
$Z$	.....	40.9	40.2	38.7	37.4	.....
$n_D^{20}$	.....	1.4160	1.4275	1.4510	1.4728	.....
$\Delta$	.....	83.2	93.8	117.4	137.8	.....
$\delta$	.....	112	123	147	166	.....
Toluene, % (from Table III)	.....	16	29	57	79	.....
Deviation	.....	+3.9	+2.0	+2.3	+1.3	.....
By Pulfrich						
$n_D^{20}$	1.4070	1.4158	1.4275	1.4510	1.4728	1.4477
$\Delta$	72.3	80.9	92.2	115.8	136.9	109.7
$\delta$	99.1	108.7	121.2	145.1	164.8	138.6
Toluene, % (from Table III and corrections)	0.0	11.9	27.0	55.0	77.5	.....
Deviation	0.0	-0.2	0.0	+0.2	-0.2	.....

TABLE VII. AROMATIC-FREE OLEFIN SERIES

	No. 75-A	No. 75-B	No. 81-C	No. 81-D
Weight %				
<i>n</i> -Heptane	46.25	33.59	24.66	12.79
Cyclohexane	44.66	32.42	23.66	12.27
2-Ethylhexene-1	9.09	33.99	51.68	74.94
$d_4^{20}$	0.7271	0.7324	0.7363	0.7420
Bromine No. (experimental)	11.7	42.5	64.6	93.4
By Abbé				
$Z$	41.2	40.9	40.8	40.6
$n_D^{20}$	1.4053	1.4093	1.4122	1.4164
$\Delta$	77.5	82.2	83.8	87.1
$\delta$	107	112	114	117
$\delta$ corrected	105	105	104	102
By Pulfrich				
$n_D^{20}$	1.4056	1.4092	1.4129	1.4164
$\Delta$	71.9	76.9	80.0	83.5
$\delta$	98.9	105.0	108.6	112.5
$\delta$ corrected	97.0	98.2	98.3	97.5
Deviation from base value of $\delta = 96.8$	+0.2	+1.4	+1.5	+0.7

base value of 98 seems to be preferable and in accurate analysis it may be actually determined, as described below.

Table III, which is recommended for use in the analysis of gasolines, was constructed from the above equations by calculating the proportional change when the base value of the saturates is changed. For example, in the case of benzene the new specific dispersion of the mixture with 98 as the base was calculated from the following equation:

$$\delta_{\text{new mixt.}} = \left( \frac{\delta_{\text{old mixt.}} - 96.9}{190.1 - 96.9} \right) (190.1 - 98) + 98$$

It is reasonable to assume that the same deviation from a straight line will hold also, in first approximation, for mixtures of paraffins and naphthenes, particularly in natural gasolines and naphthas where possible individual constitutional effects are obliterated by the numerous other constituents.

Corrections are also given in Table III to be added to the values with a change in the base value. These tables become useful if one desires to determine the actual base value for the saturated mixture by removing the aromatics and unsaturates with sulfuric acid, sulfur dioxide, or by other methods. This procedure, however, is necessary only if very accurate analysis in the low aromatic concentration range is desired.

### Selection of Specific Dispersion of Individual Aromatic Cuts

In Table X a comparison of specific dispersion values of benzene, toluene, ethylbenzene, and the xylenes by different authors is given. The results are in fair agreement and in calculations preference was given the authors' values since the purity of their compounds is known and, particularly, the data were corrected to their standard temperature of 20° C.

The value of 179.2 for the pure aromatics in the case of the xylenes and ethylbenzene was obtained by making a weighted average of the values for the four isomers.

To arrive at a reasonable value for the specific dispersion of the pure aromatics in the boiling ranges 150° to 175° and 175° to 200° C., existing literature data (3, 11) were averaged for each temperature range and plotted (Figure 1) against the average boiling point. This averaging was done in view of discrepancies existing even on the same compounds as reported by different authors. The result indicates a straight-line relation at least for the lower boiling ranges, and in view of the above-mentioned discrepancies and also the relatively high average value for the range 200° to 225° C., a straight line was assumed to continue through the ranges 150° to 200° C. The values of 175 and 171 at 162.5° and 187.5° C., respectively, were then used and Equations 4 and 5 calculated. The accuracy of the method is not affected as much as might be expected by the improper selection of these two values, since a variation of 4 units in the specific dispersion of the pure aromatic in the highest boiling fraction, where the greatest error would be encountered, results in an error of only 3 per cent aromatics at the 50 per cent aromatic point and correspondingly less at lower concentrations.

Literature data on the dispersions of the higher boiling aromatics are highly erratic and additional accurate measurements on these compounds are very desirable.

### Effect of Double Bond and Relation between Specific Dispersion and Unsaturation

The effect of increasing double bond concentration on specific dispersion is shown in Figure 3, which is based on data obtained with a mixture of 2-ethylhexene-1, *n*-heptane, and cyclohexane and correlated in Table VII. The bromine numbers were determined by the Francis method (2). As will be noted, the points fall on a straight line.

The general relation is illustrated in Figure 4. Here the specific dispersion increments—i. e., the increase in the specific dispersion above the value for the saturated hydrocarbon—of mono- and diolefins, straight-chain and cyclic, are plotted against the bromine number. These data are taken from the literature values of Ward and Kurtz (Table XI) and the authors' Table I. Theoretical bromine numbers and average values for the specific dispersion increment were used. (A discussion as to whether the Francis or other bromine method is an accurate measure of unsaturation or should be replaced by other methods is outside the scope of this paper and will be discussed in a future publication.)

In view of these considerations and the uncertainty of the



TABLE VIII. BENZENE SERIES CONTAINING OLEFINS

	No. 70-A	No. 70-B	No. 70-C	No. 70-D	No. 71-A	No. 71-B	No. 71-C	No. 71-D
Weight %								
Benzene	10.76	27.16	49.53	72.89	8.67	21.70	38.60	56.92
n-Heptane	37.21	29.24	20.07	9.08	29.97	23.35	15.64	7.09
Cyclohexane	42.54	33.51	22.59	10.66	34.26	26.77	17.60	8.32
2-Ethylhexene-1	9.49	10.09	7.81	7.37	27.10	28.18	28.16	27.67
d <sub>4</sub> <sup>20</sup>	0.7427	0.7628	0.7935	0.8309	0.7437	0.7602	0.7824	0.8108
Bromine No. (experimental)	11.8	12.9	8.8	9.3	34.1	35.3	34.4	34.9
By Abbé								
Z	40.9	39.9	38.7	37.2	40.7	40.0	39.0	37.9
n <sub>D</sub> <sup>20</sup>	1.4148	1.4274	1.4466	1.4704	1.4158	1.4260	1.4402	1.4579
Δ	82.8	98.1	116.8	136.4	85.7	96.4	111.9	129.0
δ	111	128	147	164	115	127	143	159
δ corrected	109	126	146	162	110	121	137	153
Benzene, % (from Table III)	13	32	54	71	14	27	44	62
Deviation	+2.2	+4.8	+4.5	-1.9	+5.3	+5.3	+5.4	+5.1
By Pulfrich								
n <sub>D</sub> <sup>20</sup>	1.4145	1.4274	1.4464	1.4700	1.4156	1.4259	1.4401	1.4575
Δ	80.3	93.5	113.1	137.1	81.9	92.3	107.0	124.8
δ	108.2	122.6	142.5	165.0	110.1	121.4	136.8	153.9
δ corrected	106.3	120.5	141.1	163.5	104.7	115.8	131.3	148.3
Benzene, % (from Table III and corrections)	10.9	26.5	49.4	73.0	9.1	21.7	38.8	57.1
Deviation	+0.1	-0.7	-0.1	+0.1	0.4	0.0	+0.2	+0.2

TABLE IX. TOLUENE SERIES CONTAINING OLEFINS

	No. 72-B	No. 72-D	No. 73-B	No. 73-D	No. 80-A	No. 80-B	No. 80-C	No. 80-D
Weight %								
Toluene	24.50	71.48	20.09	56.67	75.00	49.90	26.73	88.60
2,2,4-Trimethylpentane	31.14	9.74	25.54	7.72	0	0	0	0
Methylcyclohexane	35.08	10.76	28.76	8.54	0	0	0	0
2-Ethylhexene-1	9.28	8.02	25.61	27.07	25.00	50.10	73.27	11.40
d <sub>4</sub> <sup>20</sup>	0.7603	0.8236	0.7580	0.8066	0.8338	0.8033	0.7767	0.8513
Bromine No. (experimental)	11.5	9.7	32.5	33.6	30.9	62.8	91.0	14.1
By Abbé								
Z	40.3	37.5	40.0	38.2	37.2	38.4	39.3	36.6
n <sub>D</sub> <sup>20</sup>	1.4270	1.4681	1.4258	1.4574	1.4748	1.4552	1.4384	1.4864
Δ	93.9	136.1	96.4	124.9	140.9	121.7	106.3	150.5
δ	123	165	127	155	169	152	137	177
δ corrected	121	163	122	150	164	142	122	175
Toluene, % (from Table III)	27	76	28	61	77	52	28	89
Deviation	+2.5	+4.5	+7.9	+4.3	+2.0	+2.1	+1.3	+0.4
By Pulfrich								
n <sub>D</sub> <sup>20</sup>	1.4268	1.4680	1.4258	1.4573	1.4748	1.4549	1.4382	1.4863
Δ	91.8	132.3	91.1	122.0	139.1	120.3	104.5	150.0
δ	120.7	160.6	120.2	151.3	166.8	149.7	134.5	176.1
δ corrected	118.9	159.0	115.0	145.9	161.9	139.7	119.9	173.8
Toluene, % (from Table III and corrections)	24.1	70.9	19.5	56.0	74.2	48.9	25.2	87.8
Deviation	-0.4	-0.6	-0.6	-0.7	-0.8	-1.0	-1.5	-0.8

purity of the compounds, the straight-line relation seems reasonable. The agreement seems to be better with the olefins boiling in the gasoline range—i. e., bromine numbers 114 to 228. The slope of the lines of Figures 3 and 4 is approximately 0.16. The correction factor for olefins, diolefins, and unsaturated cyclics would therefore be equal to 0.16 × bromine number and the corrected specific dispersion to be used in connection with Table III would then be:

δ<sub>cor.</sub> = δ<sub>mixt.</sub> - 0.16 × bromine number

For testing the above principle, a number of synthetic samples were made by adding 2-ethylhexene-1 to various mixtures of benzene, n-heptane, and cyclohexane, and toluene, 2,2,4-trimethylpentane, and methylcyclohexane. The results are given in Tables VIII and IX. The agreement is in general very good with the maximum deviation of ±1.5 per cent aromatics and average (±) deviations much less.

Additional data on the dispersions of unsaturates whose purity has been checked just previous to the dispersion measurement are very desirable in order to establish a more exact correction factor for these classes of compounds.

In general, the dispersion method is more accurate for mixtures high in aromatics and low in olefins than for the reverse case.

Analysis of Mixtures Containing Conjugated Diolefins

Conjugated diolefins have substantially higher specific dispersions than the unconjugated compounds, as can be seen from Table XII. Traces of conjugated diolefins will not appreciably affect the accuracy of aromatic determinations.

TABLE X. SPECIFIC DISPERSION OF AROMATICS AT 20° C.

Reference	Benzene	Toluene	Ethylbenzene	o-Xylene	m-Xylene	p-Xylene
δ	189.3	184.8	175.9	180.1	181.9	178.3
6	189.0	185.0	176.0	181.0	183.0	183.0
G. W.	190.2	184.9	174.7	179.7	181.3	181.9

Fortunately, mixtures containing substantial quantities of conjugated diolefins are comparatively rare, since they are produced under drastic temperature conditions. Practically, therefore, in a series of routine samples from a common source, usually only one representative sample will have to be checked for their presence.

The same applies to an even greater degree to aromatic olefins of the styrene type which have high specific dispersions (for instance styrene Δ<sup>20°</sup> = 237.5, δ<sup>20°</sup> = 262.0) in view of the exalting effect of an aromatic double bond in conjugation with an aliphatic double linkage.

If conjugated diolefins are present in large amounts, they have to be eliminated from the sample in order not to affect the determination of aromatics. This can be readily achieved by means of the Diels-Alder reaction with maleic anhydride; the latter forms addition compounds of the type

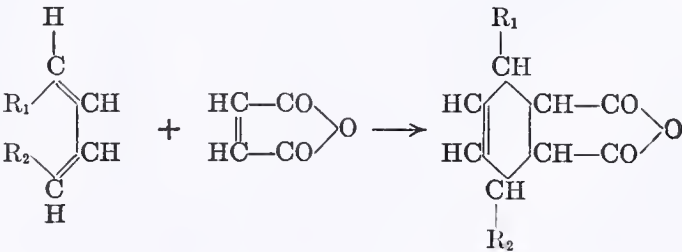




TABLE XI. SPECIFIC DISPERSION OF UNSATURATES

Hydrocarbon	N. B. P. ° C.	Theoretical Bromine No.	$\delta^a$	$\delta_{\text{sat.}}$	$\delta_{\text{unsat.}} - \delta_{\text{sat.}}$
Monoolefins					
Pentene-2 ( <i>cis</i> )	36	227.9	134	97.9	36
2-Methylbutene-2	38	227.9	135	98.3	37
4-Methylpentene-1	54	189.9	124	99.2	25
3-Methylpentene-2 ( <i>cis</i> )	66	189.9	130	96.9	33
3-Methylpentene-2 ( <i>trans</i> )	68	189.9	130	96.9	33
2-Methylpentene-2	67	189.9	130	99.2	31
Hexene-2	68	189.9	132	98.6	33
2,4-Dimethylpentene-2	83	162.8	125	98.7	26
3-Ethylpentene-2	95	162.8	126	96	30
Heptene-1	95	162.8	123	98.6	24
3-Ethylhexene-3	119	142.4	123	99	24
4-Methylheptene-3	119	142.4	125	99	26
2-Propylpentene-1	119	142.4	124	97.5	26
Octene-1	124	142.4	119	98.2	21
Octene-2	...	142.4	121	98.2	23
3-Ethylheptene-3	142	126.6	121	96	25
2,7-Dimethyloctene- <i>x</i>	160	113.9	119	99	20
4-Propylheptene-3	161	113.9	120	99 <sup>b</sup>	21
Decene-1	163	113.9	118	100	18
4-Propyldecene-3	221	87.7	116	98	18
5-Butylnonene-3	85 <sup>b</sup>	87.7	115	97	18
Cetene	274	71.2	108	98	10
3-Ethyltetramethyldecene-2	144 <sup>b</sup>	71.2	110	99 <sup>b</sup>	11
2-Methylpentamethyldecene-1	...	71.2	107	99 <sup>b</sup>	8
Diiolefins (Unconjugated)					
2,6-Dimethylheptadiene- <i>x,x</i>	144	257	140	99 <sup>c</sup>	41
2,6-Dimethylheptadiene-1, <i>x</i>	144	257	143	99 <sup>c</sup>	44
2,6-Dimethyloctadiene- <i>x,x</i>	163	231	135	97	38
2,6-Dimethyloctadiene- <i>x,x</i>	...	231	140	97	43
Unsaturated Cyclics					
Cyclohexene	83	194.6	119	96	23
1,1-Dimethylcyclohexene-3	120	145.1	116	96 <sup>c</sup>	20
1,2-Dimethylcyclohexene-3 and 4	125	145.1	114	96 <sup>c</sup>	18
1,3-Dimethylcyclohexene-3	125	145.1	119	96 <sup>c</sup>	23
1,3-Dimethylcyclohexene-4	127	145.1	122	96 <sup>c</sup>	26
1,3-Dimethylcyclohexene-5	127	145.1	119	96 <sup>c</sup>	23
1,4-Dimethylcyclohexene-1	127	145.1	117	96 <sup>c</sup>	21
1-Ethylcyclohexene-1	136	145.1	117	96 <sup>c</sup>	21
1,2-Dimethylcyclohexene-1	136	145.1	121	96 <sup>c</sup>	25
1,1,2-Trimethylcyclohexene-4	139	128.7	118	96 <sup>c</sup>	22
1,3-Dimethyl-2-ethylcyclopentene-1	140	128.7	120	96 <sup>c</sup>	24
1,1,4-Trimethylcyclohexene-3	140	128.7	117	96 <sup>c</sup>	21
1,3,5-Trimethylcyclohexene- <i>x</i>	140	128.7	121	96 <sup>c</sup>	25
1,2,5-Trimethylcyclohexene-4	145	128.7	117	96 <sup>c</sup>	21
1,1,2-Trimethylcyclohexene-2	149	128.7	117	96 <sup>c</sup>	21
1,2,3-Trimethylcyclohexene-4	150	128.7	120	96 <sup>c</sup>	24
1,2-Diethylcyclopentene- <i>x</i>	152	128.7	116	96 <sup>c</sup>	20
1-Isopropylcyclohexene-1	156	128.7	116	96 <sup>c</sup>	20
1-Methyl-2,5-diethylcyclopentene-1	164	115.6	119	96 <sup>c</sup>	23
1,2,4,5-Tetramethylcyclohexene-1	166	115.6	120	96 <sup>c</sup>	24
1-Methyl-4-isopropylcyclohexene-3	169	115.6	116	96 <sup>c</sup>	20
1,2,5-Triethylcyclopentene-1	182	104.9	116	96 <sup>c</sup>	20
1,3,4-Trimethyl-1-isopropylcyclohexene-3	78 <sup>b</sup>	96	112	96 <sup>c</sup>	16
<sup>a</sup> $\delta$ values from Ward and Kurtz (11). <sup>b</sup> At 10 mm. <sup>c</sup> Assumed.					

TABLE XII. SPECIFIC DISPERSION OF CONJUGATED DIOLEFINS<sup>a</sup>

Hydrocarbon	N. B. P., ° C.	Theoretical Bromine No.	$\delta_{\beta-\alpha}$
Conjugated Diolefins			
2-Methylbutadiene-1,3 (isoprene)	34.6	470	225
Pentadiene-1,3	43	470	243
2,3-Dimethylbutadiene-1,3	70	389	200
2-Methylpentadiene-2,4	76	389	226
2-Methylpentadiene-1,3	76	389	226
Hexadiene-2,4 (low boiling)	76	389	222
3-Methylpentadiene-1,3	78	389	225
Hexadiene-2,4 (high boiling)	79	389	232
2,3-Dimethylpentadiene-1,3	93	333	208
2-Methylhexadiene-2,4	104	333	226
Heptadiene-2,4	105	333	214
2-Methylheptadiene-3,5	117	291	206
4-Methylheptadiene-2,4	132	291	200
7-Methyloctadiene-2,4	149	257	197
4-Methyloctadiene-3,5	150	257	204
Conjugated Unsaturated Cyclics			
Cyclopentadiene	40	485	164
Cycloheptadiene-1,3	121	340	185

<sup>a</sup> Literature data of Ward and Kurtz (11).

The reaction has already been applied for the removal, identification, or quantitative determination (butadiene-1,3) of conjugated diolefins in hydrocarbon mixtures (5, 6, 9).

The authors found in a preliminary investigation that the complete removal may usually be effected by heating the sample with 20 to 30 weight per cent of maleic anhydride in a sealed tube for 1 hour at 95° to 100° C. The procedure was to seal a 5- to 15-cc. sample in a test tube cooled by solid carbon dioxide and containing the anhydride and then heating it in a boiling water bath. After the reaction, the test tube was cooled in solid carbon dioxide, its tip broken off, and the whole tube slid down into a small distilling flask whence the total liquid content was distilled over into a trap cooled by solid carbon dioxide.

A decrease in bromine number of a sample after maleic anhydride treatment is a simple and definite criterion for the presence of conjugated diolefins and in all doubtful cases



TABLE XIII. MIXTURES CONTAINING CONJUGATED DIOLEFINS

Weight % Aromatics Benzene Toluene Paraffins <i>n</i> -Heptane 2,2,4-Trimethylpentane Naphthenes Cyclohexane Methylcyclohexane Olefins 2-Ethylhexene-1 Conjugated diolefins 2-Methylbutadiene-1,3 2-Methylpentadiene-1,3	Experiment 1			Experiment 2			Experiment 3			Experiment 4				
	Diolefin-containing mixture No. 78-B	After maleic anhydride treatment	Original or diolefin-free mixture No. 71-D	Diolefin-containing mixture No. 78-D	After maleic anhydride treatment First	Second	Original or diolefin-free mixture No. 72-D	Diolefin-containing mixture No. 77-B	After maleic anhydride treatment First	Check	Original or diolefin-free mixture No. 71-C	Diolefin-containing mixture No. 77-A	After maleic anhydride treatment	Original or diolefin-free mixture No. 71-C
d <sub>4</sub> <sup>20</sup>	44.93	60	56.92	0	.....	.....	0	30.63	42	42	38.60	29.75	41	38.60
n <sub>D</sub> <sup>20</sup>	0	.....	0	65.23	70	69	71.48	0	.....	.....	0	0	.....	0
Bromine No. (experimental)	5.60	.....	7.09	0	.....	.....	0	12.41	.....	.....	15.64	12.05	.....	15.64
Z	0	.....	0	8.89	.....	.....	9.74	0	.....	.....	0	0	.....	0
Δ (Abbé)	6.57	.....	8.32	0	.....	.....	0	13.97	.....	.....	17.60	13.56	.....	17.60
Δ (Abbé)	0	.....	0	9.82	.....	.....	10.76	0	.....	.....	0	0	.....	0
δ (Abbé)	21.83	.....	27.67	7.32	.....	.....	8.02	22.34	.....	.....	28.16	21.71	.....	28.16
	0	.....	0	0	.....	.....	0	10.43	.....	.....	0	22.93	.....	0
	21.07	.....	0	8.74	.....	.....	0	10.22	.....	.....	0	0	.....	0
	0.7888	0.8148	0.8108	0.8138	0.830	0.8284	0.8326	0.7640	0.7838	0.7812	0.7824	0.7559	0.782	0.7824
	1.4550	1.4586	1.4579	1.4661	1.4678	1.4660	1.4681	1.4376	1.4394	1.4380 <sup>a</sup>	1.4402	1.4328	1.438	1.4402
	97.5	32.3	34.9	36.3	9.4	9.1	9.7	97.0	30.2	36.3	34.4	109.1	40.7	34.4
	37.2	37.9	37.9	37.3	37.7	37.6	37.5	38.3	39.0	39.0	39.0	38.4	39.0	39.0
	138.6	129.2	129.0	138.4	133.1	134.3	136.1	121.1	111.7	111.5	111.9	119.1	111.5	111.9
	175.7	159	159	170	163	162	165	159	143	143	143	158	143	143

<sup>a</sup> Actual weight per cent of material (diolefin) removed was 23% (theory 21%).

<sup>a</sup> Actual weight per cent of material (diolefin) removed was 23% (theory 21%).

such a check is recommended; this difference in bromine number before and after treatment also gives the weight per cent of conjugated diolefins in the sample.

Results obtained by the maleic anhydride method are correlated in Table XIII. Mixtures of paraffins, naphthenes, olefins, and aromatics were prepared with the conjugated diolefins—isoprene and/or 2-methylpentadiene-1,3.

It can be seen by comparing the bromine number and other properties of the middle column of each experiment with the corresponding values of the original diolefin-free mixture that the diolefins have been practically completely removed. The aromatic content of the treated mixture, as determined by the Abbé refractometer, is in excellent accord with that of the original or diolefin-free mixture.

A repetition of the treatment, as shown in experiment 2, does not change, within experimental error, either the bromine number or the specific dispersion.

In experiment 3 a check was run and also the weight per cent of diolefin removed was determined directly by the increase in weight of the anhydride. Again full agreement with the first determination and the requirement of theory is observed.

Still further work on synthetic mixtures and conjugated diolefinic gasolines is desirable.

### Effect of Oxygen, Sulfur, Nitrogen, and Halogen Compounds on Accuracy of Method

The present method is recommended for pure hydrocarbon mixtures, and tests for other elements should be made if suspected. However, since oxygen, sulfur, nitrogen, and halogen

TABLE XIV. OXYGEN, NITROGEN, SULFUR, AND HALOGEN COMPOUNDS

	N. B. P. ° C.	$d_4^{20}$	$n_D^{20}$	$\Delta_{H\beta-H\alpha}$	$\delta$
Oxygen Compounds					
Methyl alcohol	64.5	0.792	1.329	54	68.1
Ethyl alcohol	78.5	0.7893	1.361	61	77.2
<i>n</i> -Propyl alcohol	97.8	0.804	1.386	66	82.0
<i>n</i> -Heptyl alcohol	175.8	0.819	1.425	74	90.4
Ethylene oxide	10.7	0.8877	1.35977	587	65.37
Ethyl ether	34.5	0.714	1.3526	61	85.4
<i>n</i> -Propyl ether	89	0.747	1.3807	66	88.3
Phenol	182	1.05741	1.542541	18941	178.841
Benzyl alcohol	205.8	1.046	1.5399	173	165.3
<i>o</i> -Cresol	190.8	1.051	1.547	185	176.0
Furan	31	0.937	1.4216	113	120.5
2,5-Dimethyl furan	94	0.888	1.435121.6	114	128.3
Nitrogen Compounds					
Methyl cyanide	82	0.783	1.3474	58	74.0
Ethyl cyanide	97.1	0.783	1.3664	60	76.6
<i>n</i> -Propylamine	48.7	0.719	1.389	74	102.9
<i>n</i> -Butylamine	76	0.740	1.401	75	101.3
Triethylamine	89.5	0.728	1.401	81	111.2
Aniline	184.4	1.022	1.5863	249	243.6
Benzylamine	184	0.980	1.5440	175	178.5
Methylaniline	195.7	0.986	1.5714	249	252.5
Pyridine	115.3	0.982	1.509	163	165.9
Piperidine	105.8	0.860	1.4530	89	103.4
Sulfur Compounds					
Ethyl mercaptan	34.7	0.839	1.4306	102	121.5
Isobutyl mercaptan	88	0.836	1.4386	97	116.0
Isoamyl mercaptan	129.5	0.835	1.4412	91	108.9
Diethyl sulfide	91.6	0.837	1.4425	99	118.5
Diethyl disulfide	153	0.993	1.5063	130	130.9
Thiophene	84	1.065	1.5285	173	162.4
Thiophenol	168.69	1.07423	1.586123	23123	215.623
Halogen Compounds					
Carbon tetrachloride	76.8	1.595	1.4607	97	60.8
Chloroform	61.2	1.489	1.4467	89	59.7
<i>n</i> -Butyl bromide	101.6	1.275	1.4398	89	69.8
<i>n</i> -Butyl chloride	78	0.884	1.4015	71	80.3
<i>n</i> -Butyl iodide	127	1.617	1.5001	140	86.5
Bromobenzene	156.2	1.497	1.560	193	128.9
Chlorobenzene	132.1	1.107	1.525	172	155.3
Iodobenzene	188.6	1.832	1.621	253	138.1
<i>o</i> -Dichlorobenzene	179	1.298	1.549	176	135.5

<sup>a</sup> At 20° C. unless indicated.



compounds in small amounts are always possible constituents of natural and to a less extent of refined gasolines and naphthas, it is worth while to know the effect these would exert upon this method of analysis.

In Table XIV are listed a number of organic compounds containing the above constituents. These data were taken from the International Critical Tables. A survey of this table shows the specific dispersion to bear a similar relation to the carbon skeleton as found in hydrocarbons—for example, the specific dispersions of the phenols (176 to 179), thiophenol (216), and anilines (243 to 252) are much higher than the aliphatic alcohols (68 to 82), mercaptans (109 to 122), and alkylamines (101 to 111). That aromaticlike, heterocyclic systems have substantially higher specific dispersions than the saturated systems is well brought out by comparison of pyridine (166), thiophene (162), and furan (121), with piperidine (103), diethyl sulfide (119), and ethyl ether (85), respectively. (The two latter compounds may be taken as the closest analogies to tetrahydrothiophene and tetrahydrofuran, for which data are lacking.)

In general, the specific dispersions are of the same order of magnitude as similar types of hydrocarbons and none are exceptionally high. Practically, it may be expected that paraffinic and naphthenic gasolines will contain mainly aliphatic, oxygen, sulfur, nitrogen, or halogen derivatives, while aromatic gasolines will, correspondingly, contain aromatic or heterocyclic derivatives of these elements. It would be logical to consider the latter as "aromatics," just as any unsaturated oxygen, sulfur, nitrogen, or halogen compounds will be determined as "unsaturates." In view of this, and the fact that when present in gasolines the compounds are present in only small quantities (less than 1 to 2 per cent) it may safely be concluded that they will not affect the accuracy of the method.

A simple calculation shows that 0.1 per cent of sulfur, in the form of ethyl mercaptan, monosulfide, or disulfide, will raise the determined amount of benzene in a 25.0 weight per cent mixture with saturated hydrocarbons by 0.04, 0.06, and 0.12 weight per cent, respectively. The same amount of sulfur in the form of thiophenol (0.35 weight per cent) will raise the benzene content by 0.37 weight per cent, practically in complete agreement with the total aromatic ring content.

In general, oxygen compounds will lower and nitrogen and sulfur compounds will raise the specific dispersion of hydrocarbon mixtures.

TABLE XV. TEMPERATURE COEFFICIENTS

	$\frac{dn_D}{dt}$	$\frac{dn_{H\beta}}{dt}$	$\frac{dn_{H\alpha}}{dt}$	$\frac{d\Delta}{dt}$	$\frac{d\delta}{dt}$
Benzene	-0.03618	-0.03635	-0.03611	-0.2482	-0.051
Toluene	-0.03529	-0.03540	-0.03519	-0.2107	-0.048
n-Heptane	-0.03462	-0.03469	-0.03458	-0.1095	-0.037
2,2,4-Trimethylpentane	-0.03465	-0.03476	-0.03465	-0.1070	-0.031
Cyclohexane	-0.03501	-0.03505	-0.03494	-0.1163	-0.034
Methylcyclohexane	-0.03462	-0.03466	-0.03454	-0.1135	-0.039

### Effect of Temperature on Dispersion and Specific Dispersion

The effect of temperature on specific dispersion is small and has usually been disregarded by previous workers, but for precision work it has to be taken into consideration. The authors have determined the specific dispersions of different types of hydrocarbons at 20° and 80° C. (see Table I). The calculated temperature coefficients of both the dispersion and specific dispersion are collected in Table XV.

The paraffins and naphthenes have dispersion temperature coefficients about one half that of the aromatics—i. e., ap-

proximately 0.11 and 0.23, respectively. The values for the specific dispersion temperature coefficient are also higher for the aromatics, although the difference is not so marked as in the case of the dispersion coefficients.

It is now possible accurately to convert dispersions and specific dispersions measured at some other temperature to the authors' standard temperature of 20° C.

As a first approximation, which is substantiated by unpublished data on high boiling compounds, the specific dispersion decreases linearly with temperature over this temperature range.

When an Abbé refractometer is used for the measurements at about room temperature (20° to 30°), it is not necessary to make the temperature correction, since the error in the measurement is greater than the correction. However, when Pulfrich measurements are made, it is advisable to make this correction. All measurements as given in the authors' tables were corrected on the above data.

TABLE XVI. COMPARISON OF SULFURIC ACID ABSORPTION AND DISPERSION METHODS OF ANALYSIS

Gasoline and Naphtha Sample (Bromine No. 0.0)	Weight Per Cent of Aromatics	
	By $H_2SO_4$	By specific dispersion
1	12	8
2	30	28
3	34	28
4	21	21
5	33	30

### Results with Gasolines and Naphthas

A critical comparison of the accuracy and reliability of this method with other methods of aromatic determination will be made in another paper. However, a comparison with the most commonly used method—namely, extraction with concentrated 96 per cent sulfuric acid—is important and is shown in Table XVI.

The sulfuric acid method is at best reliable only for olefin-free mixtures. In the presence of olefins, as has been shown by Ipatieff and Pines (4), serious complications (alkylation of aromatics, polymerization, and paraffin formation) occur. In view of this, gasoline and naphtha samples containing only aromatics and saturated hydrocarbons were used.

A comparison of the data in columns 2 and 3 shows a reasonable agreement for most practical purposes. Owing to the solubility of saturated hydrocarbons in sulfuric acid, slightly higher values are obtained by the chemical method.

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# Manganese and Chromium in Steel

## Modified Persulfate-Arsenite Method

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THE persulfate-arsenite method for manganese is widely used in routine analysis of steel, since it is rapid, economical, and clean as compared with the alternative bismuthate method. In solutions as normally used, arsenite reduces septivalent manganese to more or less midway between the trivalent and quadrivalent state. Consequently the method suffers in reliability, since standardization is empirical and varies with the operator, and the end point is indefinite, particularly in the presence of sexivalent chromium.

Lang (3) found that the use of catalysts such as potassium iodide and iodate causes the reduction of permanganic acid by arsenite to proceed quantitatively to the bivalent condition in sulfuric or hydrochloric acid solutions. Bright (1) confirmed this and showed that arsenious oxide could be used as a direct primary standard in permanganimetry. Gleu (2) proposed the use of a 0.01 *M* solution of osmium tetroxide as catalyst, and Park (4) investigated and found satisfactory the use of this catalyst for evaluating manganese in steel by the bismuthate procedure, using arsenite as reducing agent.

In the present work it has been shown that osmium tetroxide is a suitable catalyst for the persulfate-arsenite method for manganese in steel. Potassium iodide and iodate were ineffective in the same solutions, because of precipitation by silver ions; but they were successful after precipitation of silver as chloride, provided excess hydrochloric acid was present in concentrations above 1 ml. of hydrochloric acid (1 to 2) per 150 ml. of solution. However, in the presence of these catalysts chromium is reduced from the sexivalent to the trivalent state. Chromium, if present, must be evaluated separately and manganese found by deduction.

Using the routine persulfate method on Ridsdale standard steels, arsenite with osmium tetroxide as catalyst gave high results for manganese. This was found to be due mainly to a direct oxidation of arsenite by undecomposed persulfate, and not to the reoxidation of manganese by persulfate. This direct oxidizing effect in equivalents of manganese was 0.17, 0.14, and 0.07 mg. for persulfate concentrations of 2.0, 1.0, and 0.20 gram per 150 ml., respectively. For accurate work by this method, almost complete decomposition of persulfate is necessary, and this means longer boiling periods. To stabilize permanganic acid throughout this period, the following reagent concentrations (per 100 ml. of solution) were found necessary and sufficient within the usual range of manganese concentrations:

Sulfuric acid (sp. gr. 1.84)	5 ml.
Phosphoric acid (sp. gr. 1.75)	2 ml.
Persulfate	2 grams
Silver nitrate	50 mg.

In such solutions the minimum period for effective decomposition of persulfate by boiling is 4 minutes. Permanganic acid is stable after an 8-minute boiling period. Chromium, when present, was satisfactorily determined on the same solution by the usual persulfate method. For the titration of sexivalent chromium arsenite was used with a 0.0025 *M* solution of potassium iodide as catalyst. Vanadium does not interfere and this is an advantage, since the permanganate end point is not subject to the fading that must be guarded against in the presence of vanadium, when ferrous sulfate is used for reduction. Owing to its stability, it is suggested that arsenite replace ferrous sulfate for volumetric determinations of chromium and manganese. The following tabulated results

were obtained on Ridsdale steels "J" and "V", using the procedure described below; chromium was introduced where necessary by means of bichromate:

Standard Steel	Constituents Present			Constituents Found <sup>a</sup>		
	Mn Mg.	Cr Mg.	V Mg.	Mn Mg.	Cr Mg.	V Mg.
J	7.68	Nil		7.69	Nil	
J	7.68	3.54	Nil	7.71	3.51	Nil
V	5.42	8.61	2.73	5.32	8.50	2.74

<sup>a</sup> Average of three determinations.

## Manganese and Chromium on One Sample

**SOLUTIONS REQUIRED.** Silver nitrate, 10 grams dissolved in 1 liter of distilled water. Ammonium persulfate, 250 grams dissolved in water, filtered if necessary, and made up to 500 ml.

Sulfuric-phosphoric acid. Pour 1 liter of sulfuric acid into 6 liters of distilled water, and add 300 ml. of phosphoric acid (sp. gr. 1.75).

Sodium arsenite solution, 0.0316 *N*. Dissolve 7.8 grams of pure arsenious oxide in 500 ml. of distilled water and 50 ml. of sodium hydroxide (1 pound per liter). When completely in solution dilute to 5 liters with distilled water. Standardize against sodium oxalate through permanganate.

**PROCEDURE.** Transfer 1 gram of the steel drillings to a 500-ml. Erlenmeyer flask. Take up in 50 ml. of sulfuric-phosphoric acid mixture. Heat gently until in solution and then oxidize ferrous iron to ferric by adding 5 ml. of nitric acid (sp. gr. 1.20). Boil to expel oxides of nitrogen and add 50 ml. of distilled water and 5 ml. of silver nitrate solution.

Boil and add 5 ml. of ammonium persulfate solution. Boil for a further period of not less than 4 minutes and not greater than 6 minutes. Cool rapidly in a water bath to 25° C. Add 3 drops of osmium tetroxide (0.01 *M*) and then run in sodium arsenite in slight excess (5-ml. excess). Titrate excess arsenite by adding potassium permanganate dropwise to the first detectable pink tinge. The volume of arsenite so obtained represents manganese plus chromium (a).

Return solution to hot plate. Boil and add 5 ml. of persulfate solution. Boil the solution for 8 to 10 minutes, and run in 4 to 5 ml. of hydrochloric acid (1 to 3). Boil for 5 minutes after the pink color of the solution has been discharged. Cool to 25° C., add 3 drops of potassium iodate (0.0025 *M*), and run in a small excess of arsenite. Titrate to a faint pink tint with potassium permanganate. The volume of arsenite so used represents chromium (b).

By deducting (b) from (a) the manganese equivalent is obtained. For routine work the theoretical equivalent of arsenite and permanganate may be used for obtaining the permanganate equivalent of (a) and (b). However, for accurate work the volumes obtained for (a) and (b) must be corrected for dilution effect and color interference. This usually amounts to 0.2 to 0.3 ml. for chromium contents up to 1 per cent and should be added to both (a) and (b). This may be determined by boiling the solution after the final titration for 10 minutes. After cooling, the volume of potassium permanganate required to give a perceptible pink tint is noted and this volume added to both (a) and (b). Vanadium, if present, is best estimated on the solution remaining by the ferrous sulfate-persulfate method, followed by titration with potassium permanganate. In this the volume correction for dilution and color interference must be deducted from the potassium permanganate buret reading.

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# Construction of Manometers for Measuring Flow

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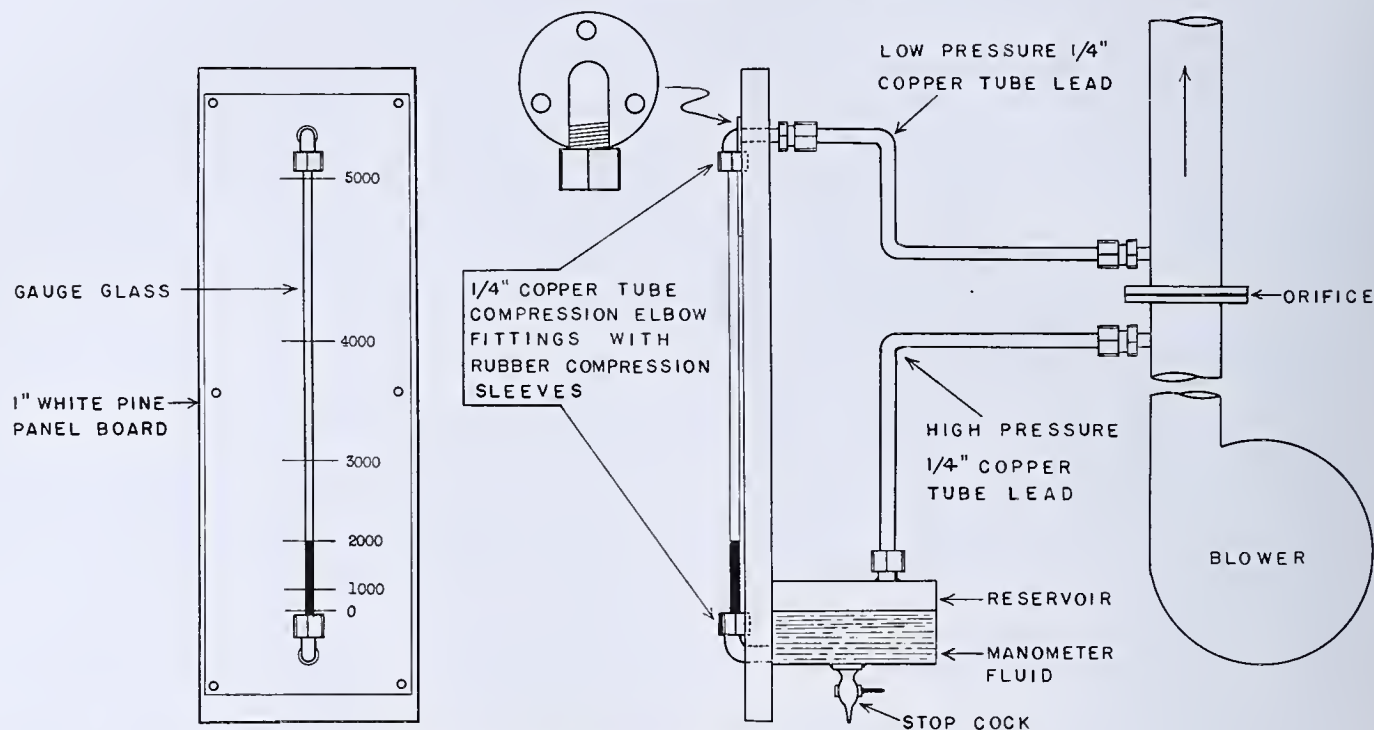


FIGURE 1. DIRECT-READING FLOW MANOMETER GAGE



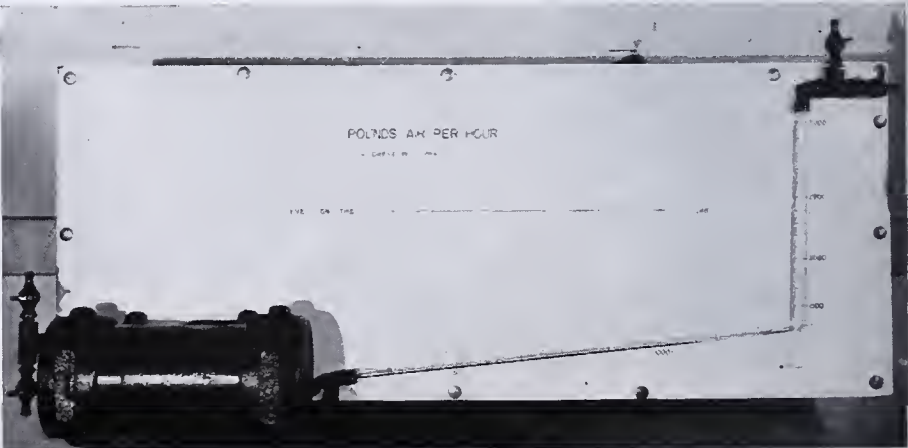
**F**LIUID flow is frequently determined by measuring the pressure drop of the fluid across an orifice or Venturi. The equal-bore U-tube manometer is the simplest device for measuring this pressure drop, but the determination requires reading the two column heights and subtracting the lesser height from the greater. The pressure drop reading also requires conversion into flow units. The several operations required to make a flow determination with an equal-bore U-tube are reduced to one operation with the direct-reading flow manometer gage shown in Figures 1 and 2. This instrument is built on the U-tube principle; however, one arm is a reservoir with a large horizontal cross section and the other arm is a small-bore glass tube. In all manometers, an external pressure difference across the instrument

FIGURE 2 (left). DIRECT-READING FLOW MANOMETER GAGE

causes the liquid in one arm to be displaced into the other, so that the difference in column heights creates a pressure equal and opposite to the external pressure. If the greater external pressure is connected to the reservoir of the manometer shown in Figure 1 and the smaller pressure to the tube, a very slight depression of the manometer liquid in the reservoir forces the liquid in the tube to the equilibrium level. In the particular instrument shown, a 0.04-cm. (0.016-inch) depression of the reservoir level causes a 75-cm. (30-inch, full-scale) rise in the tube. For practical purposes, the rise in the tube column can be considered the pressure difference reading and the flow scale plotted directly behind the tube for a given fluid density. The correction for the change in the reservoir level is a lineal function of the tube column height (assuming the cross section of the tube and reservoir constant) and is dependent upon the ratio of tube and reservoir cross-section areas.

The gage shown in Figure 1 is constructed of simple materials at very moderate cost. The reservoir consists of 0.3-cm. (0.125-inch) steel plate welded together into a box with the plate facing

FIGURE 3. DIRECT-READING MANOMETER GAGE WITH INCLINED SCALE





the gage panel extending beyond the box to accommodate the bolts that hold it to the panel board. A 0.3-cm. petcock is brazed into a hole in the bottom of the reservoir for filling and draining. A 0.6-cm. (0.25-inch) copper tubing compression elbow is brazed into a hole in the side facing the panel board, so as to project through a hole in the panel board and receive the end of the glass tube. A 0.6-cm. copper tubing compression fitting is also brazed into a hole in the top of the reservoir to receive the high-pressure lead.

The small-bore glass tube is ordinary laboratory tubing, about 6 mm. in outside diameter, and fits nicely into 0.6-cm. copper tubing compression fittings. The compression rings in the copper tubing fittings are replaced with rings cut from rubber tubing 6 mm. in inside diameter. The top of the glass tubing is received by another 0.6-cm. copper tubing compression elbow. A bracket is brazed to this elbow and holds the fitting in a hole in the panel board. The panel board is of shellacked white pine 2.5 cm. (1 inch) thick, 20 cm. (8 inches) wide, and 90 cm. (36 inches) long, cut out for the copper tubing elbows and drilled for the reservoir bolts. The scale is computed from orifice formulas (1) and plotted on tracing paper. Prints of the scale are mounted on the panel board behind the glass tube, so that the zero point is level with the midpoint of the reservoir. The manometer liquid is brought to the zero point when the gage is properly leveled.

The choice of a manometer liquid is important. When water is used as the manometer liquid in the gage shown in Figure 1, which is used to measure air flow, momentary flow fluctuations make readings difficult. A light mineral oil has sufficient viscosity to damp out these fluctuations, and, unlike water,

FIGURE 4. MANOMETER FOR MEASURING COOLING WATER FLOW

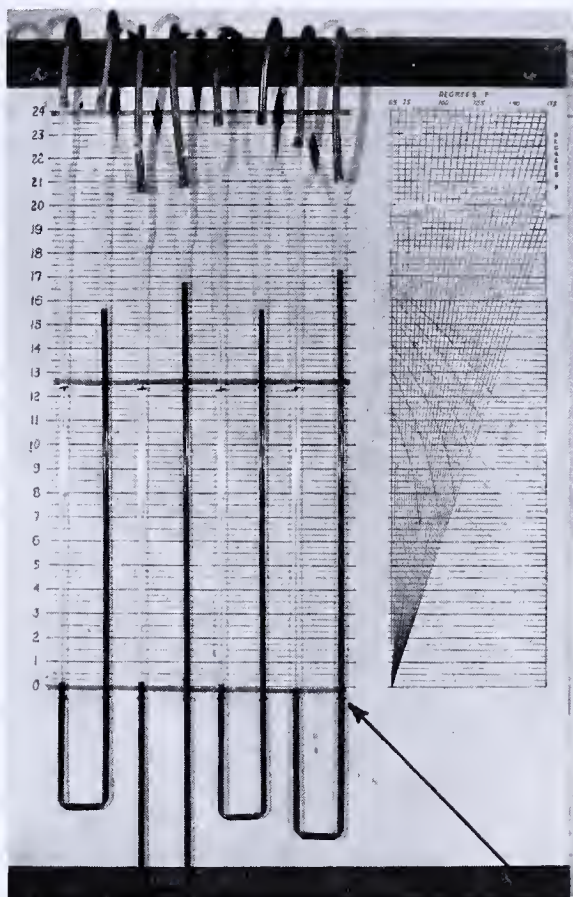
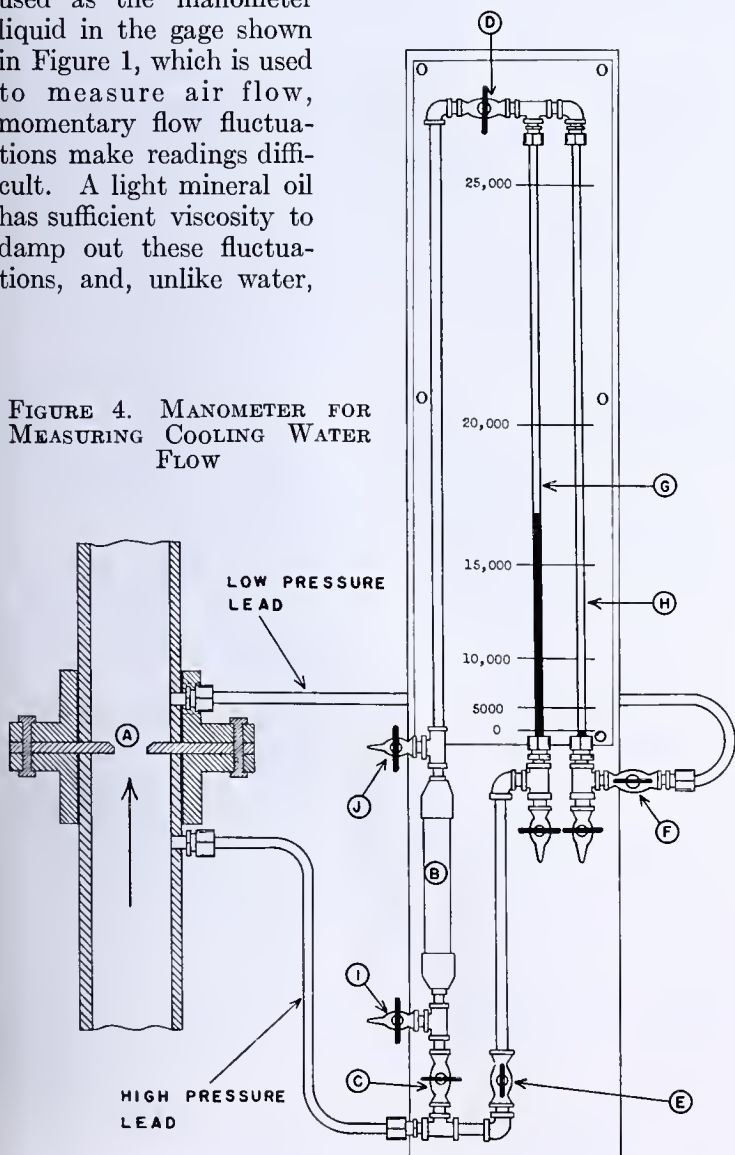
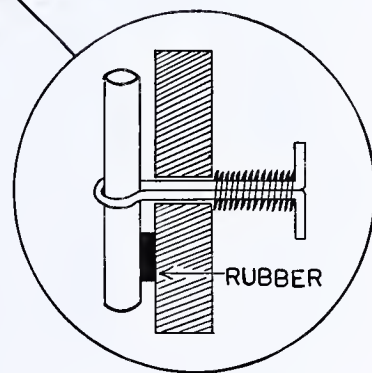


FIGURE 5. U-TUBES FOR MEASURING PERFORMANCE OF FOUR FANS OPERATING IN PARALLEL



does not freeze or evaporate. A constriction in the line will also cause dampening, but is subject to clogging from dirt. A trace of red dye added to the oil greatly facilitates gage readings.

Because the flow scale is a function of the square root of the pressure drop, the high-flow portion of the scale of a vertical tube is more sensitive to variations than the low portion. The gage shown in Figure 3 overcomes this objection by having the low portion of the scale over rise on a slope and the high portion rise vertically. A tube, bent in the shape of the curve of the following equation, will have equally spaced divisions for equal increments of flow throughout the entire range.

$$x = \sqrt{\frac{y}{4k} - y^2} + \frac{1}{4k} \sin^{-1} (2 \sqrt{ky})$$

$x$  and  $y$  are abscissa and ordinate, respectively. The constant,  $k$ , in this equation must be chosen so that the maximum value,  $y$ , is less than  $\frac{1}{4k}$ , as the curve becomes imaginary when  $y$  is greater than  $\frac{1}{4k}$ .

The manometer shown in Figure 4 was designed to measure the flow of water through an orifice and has the novel feature that the same water is used as the manometer liquid. This gage is essentially an inverted equal-bore U-tube with a pump to regulate the air pressure above the manometer water columns and thus adjust the lower level column to a scale zero point. The air pump is also operated by the water whose flow is being determined.



The operation of the gage shown in Figure 4 is as follows: From the orifice, *A*, the high-pressure lead is connected to the manometer arm, *G*, through valve *E* and to the air pump, *B*, through valve *C*. Valve *C* is opened and admits water to the pump and compresses the air in the top of the pump and U-tube. *C* is then closed and valves *E* and *F* are opened, admitting water from the high- and low-pressure orifice leads to manometer arms *G* and *H*, respectively. The level of the water in the low-pressure tube, *H*, will not rise to the zero point because the level of the pump, *B*, gives greater air pressure in the manometer than is necessary. Leaving valves *E* and *F* open, valve *I* is opened slightly, relieving some of the water trapped in pump *B* and thus the air pressure in the manometer arms, and letting the water level in the manometer tubes rise. When the water level in *H* reaches the zero point, *I* is closed and the height of the water in *G* read directly on the flow scale. Valves *D*, *I*, and *J* and the petcocks at the bottom of the manometer tubes are used to empty water from the pump and tubes.

This gage is readily made from standard pipe and copper tubing fittings. Heavy-walled rubber tubing leads and a removable orifice piping section make temporary installation convenient.

Figure 5 shows a quickly assembled set of U-tubes for measuring the performance of four fans operating in parallel.

Each U-tube is connected to the fan ducts so as to measure the static pressure across each fan. The tubes themselves are mounted on a flexboard panel with the wire slip rings shown in the

insert of Figure 5, which allows them to slip up and down like a trombone slide. In this way, the lower liquid column of each U-tube is set on the zero line of the scale behind the tubes. Rubber strips on the scale prevent the tubes from slipping.

The high liquid column is read directly on the scale which is calibrated in inches. To the right of the inch scale is a scale of cubic feet per minute delivered by the fan at standard conditions and plotted from the manufacturer's tables of fan performance at the r. p. m. used. The triangle to the immediate right of the cubic feet per minute scale is a chart which converts the reading to cubic feet per minute delivered at the temperature of the air passing through the fan or at standard conditions but corrected for the temperature of the air passing through the fan. (Laying out this chart follows directly from Charles' law. The isothermal lines are straight lines radiating from the origin with equal increments subtending equal angles.) Horizontal projection of the U-tube reading through the chart (which can be done visually) gives any of the delivery figures described above. Many fans have two possible deliveries at the same static pressure; however, only one occurs in the normal operating range, the other occurring when very little air is passing through the fan. Any static pressure measurement of fan performance would be subject to this difficulty.

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## Pressure Regulator for Dynamic Gaseous Systems

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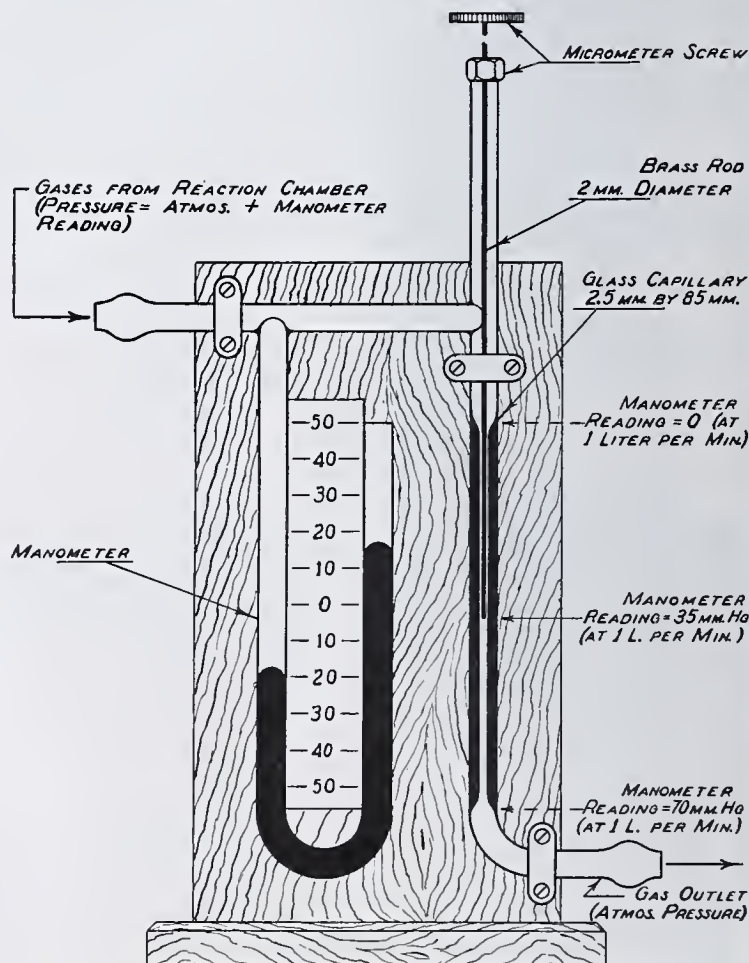
IN MANY cases where gaseous reactions are studied by the dynamic method, it is desirable to maintain pressures higher than atmospheric in the reaction chamber. While this obviously can be accomplished by bubbling the gaseous reaction products through a suitable liquid seal having a hydrostatic head equivalent to the desired pressure, this method has the following disadvantages:

1. Continuous fluctuation in pressure will occur, owing to the bubbling through the liquid.
2. The gaseous reaction products will be contaminated with the liquid through which the gas is bubbled.
3. Certain constituents of the reaction products may react with or dissolve and condense into the liquid to a greater extent than other compounds.

In order to avoid these disadvantages, a new pressure regulator has been developed. As shown in the figure, it is very simple in design and consists essentially only of a glass capillary tube 2.5 mm. in diameter and 85 mm. long and a brass rod (platinum or glass for reaction products containing corrosive gases) which is 2 mm. in diameter. By means of a micrometer screw (or a rubber stopper) the wire may be inserted to any desired extent into the glass capillary, thus increasing the frictional resistance which controls the pressure in the reaction chamber or the system.

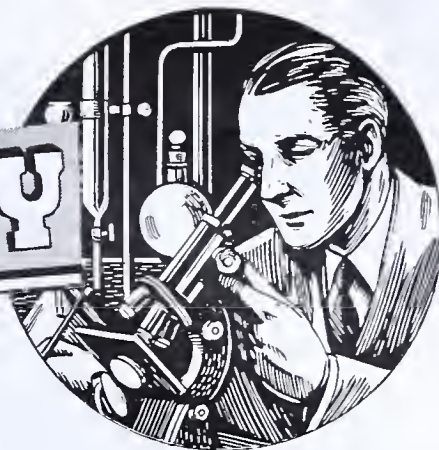
In addition to being used for maintaining various pressures in the gaseous reaction chambers, the new device may be used in the calibration of flowmeters which are to be used at pressures higher than atmospheric, or for accurate calibrations on days when the atmospheric pressure is below normal. Another application is expected to be found by investigators of gaseous reactions desiring to maintain a constant pressure throughout the series of experiments regardless of variation in atmospheric pressure. In such cases, it is believed that it will be advisable to select a pressure corresponding to the highest atmospheric pressure expected at the location of the

laboratory and then to use the above-described regulator to raise the pressure in the reaction chamber to this value in every experiment.





# MICROCHEMISTRY



## Microscopy in the Resin Industry

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TO A microscopist, the investigation of resins and their plastics is an interesting and important field because it gives him boundless opportunity to exercise his technique and his ingenuity. There are so many different natural and synthetic resins (5), each capable of assuming fluid, plastic, or elastic forms, that almost every case requires a fresh attack. Moreover, a great variety of other materials, with microscopical characteristics and optical properties, are often used as fillers or components; their distribution and identification are also important matters.

pressure. The paper is concerned with the application of micromethods, especially microscopical ones, in the study of typical resins for various commercial uses. The few illustrations given below have been chosen as typical examples of the many microscopical problems which are being investigated in the industrial research on resins.

TABLE I. PROPERTIES OF RESINS<sup>a</sup>

	Refractive Index	Specific Gravity	Brinell Hardness (2.5-Mm. Ball, 25 Kg.)
Ethyl cellulose	1.47	1.14	
Cellulose acetobutyrate	1.47		
Cellulose acetate (molded)	1.47-1.50	1.27-1.63	7 (10 kg.)
Cellulose acetate (sheet)	1.49-1.50	1.27-1.37	6-11 (10 kg.)
Methyl methacrylate	1.49	1.18	18-20 (500 kg., 10 mm.)
Ester gum (rosin-glycerol)	1.49 ±	1.08-1.09	
Acrylates	1.5	1.35-1.60	8-11 (10 kg.)
Cellulose nitrate	1.50-1.51		
Glass	1.47-1.55	2.2	0.015 (mm. deep.)
Alkyd resins (glycerol-phthalic anhydride)	1.51-1.57	1.1-1.3	
Vinyl acetate	1.53	1.34-1.36	15-25
Manila	1.53-1.54	1.06-1.08	
Casein-formaldehyde	1.54 ±		23
Rosin	1.53-1.55		
Alkyd, modified with rosin	1.54-1.56	1.11-1.14	
Shellac	1.53		
East India resins	1.538-1.543	1.00-1.06	
Damar	1.535-1.536	1.04-1.06	
Pontianak	1.540	1.07-1.08	
Boe Manila	1.539-1.540	1.07-1.08	
Sandarac	1.545	1.05-1.09	
Kauri	1.544-1.546	1.03-1.05	
Congo	1.540-1.541	1.05-1.07	
Vinyl chloride	1.54		
Urea-formaldehyde	1.54-1.6	1.48-1.50	48-54 (500 kg., 10 mm.)
Rubber (chlorinated)	1.56	1.5	
Sulfonamide-aldehyde	1.59		
Phenol-formaldehyde	1.58-1.65	1.27-1.32	30-45
Coumarone-indene	1.62-1.64		
Polystyrene	1.60-1.67	1.05-1.07	20-30
Sulfur	1.9-2.3	1.92-2.07	

<sup>a</sup> Some of these data are to be found in (2; 3, p. 384; 4).

The resin technologist welcomes a wider application of microscopical methods because they are peculiarly well adapted to the examination of his complex materials. The microscopist is often able to determine certain properties of the resin more quickly than could be done by any other method. Just as often, his methods offer the only means of determining these properties. When necessary, the adapted methods of the biologist, petrographer, colloid chemist, mineralographer, and physical tester may all be pressed into service.

In this paper, the word "resin" is taken in a broad sense to mean any essentially amorphous material which may be rendered plastic under specified conditions of temperature and

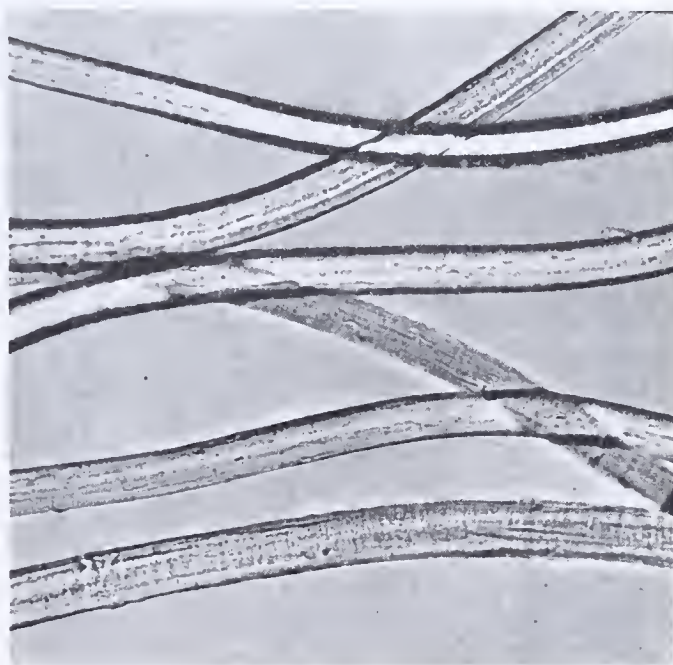


FIGURE 1. ARTIFICIAL WOOL FROM CASEIN AND FORMALDEHYDE (× 200)



FIGURE 2. CROSS SECTION OF LAMINATED PAPER, IMPREGNATED ON BOTH SIDES WITH SULFUR (× 3)



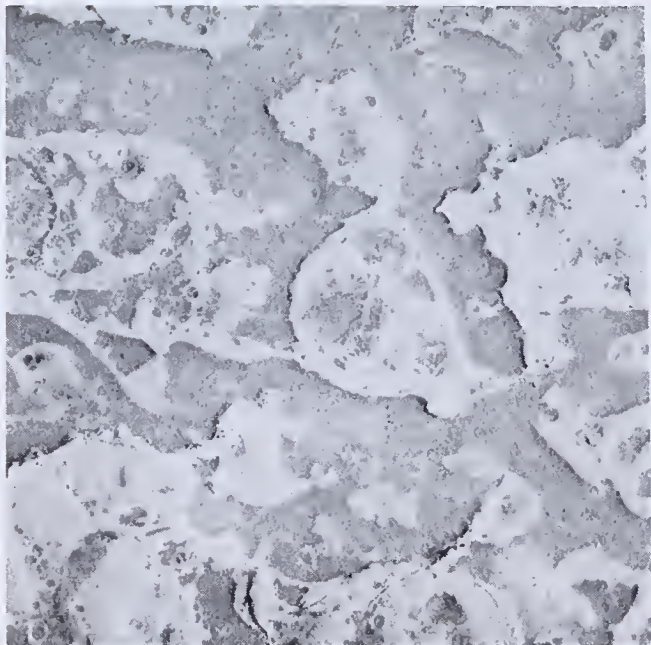


FIGURE 3. EROSION SPOTS ON AN ENAMEL AFTER ACCELERATED WEATHERING IN WEATHEROMETER ( $\times 15$ )

### Physical Properties

Refractive indices may be determined by immersion methods, provided that at least some microscopical particles may be found sufficiently free of other physical phases, like pigments and fillers. This method is much quicker and more convenient than a determination on the refractometer, which requires a relatively large, clear piece with two perpendicular surfaces, one of them polished.

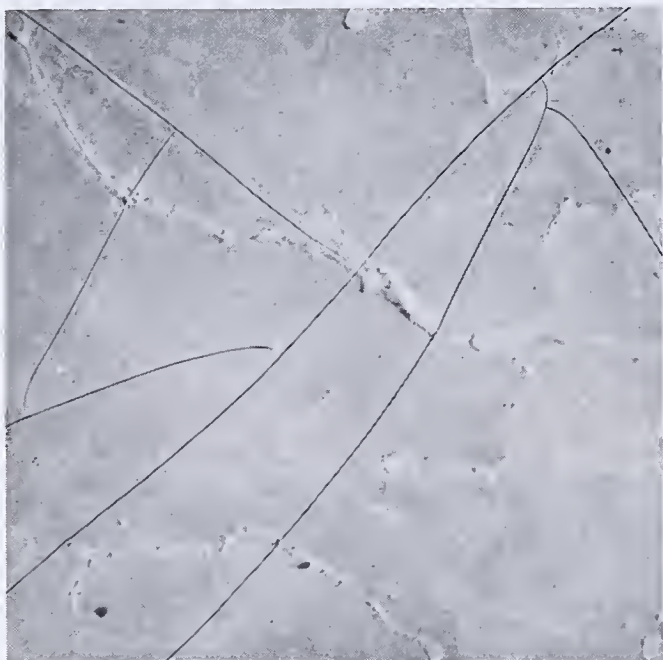


FIGURE 4. MICROSCOPIC CRACKS AND EROSION SPOTS ON BRITTLE ENAMEL AFTER ACCELERATED WEATHERING IN WEATHEROMETER ( $\times 15$ )

Specific gravity may be determined in a micro way by immersing some of the finely powdered resin in liquids of standardized specific gravity and noticing whether the particles sink or float. This procedure frequently serves also to separate out fillers and other materials which differ from the

resin in specific gravity and have been liberated from it by grinding to sufficiently small particles. Sometimes this separation is sharp enough to be approximately quantitative. The various fractions may subsequently be examined for refractive index and other microscopical properties.

It is common practice to measure the impression hardness of a substance by observing microscopically the pattern impressed upon it by some hard object of known geometric shape. Scratch hardness is also determined microscopically by measuring the width of a scratch made by a diamond point (as in the Bierbaum apparatus, patented by C. H. Bierbaum and manufactured by the Spencer Lens Co., Buffalo, N. Y.). This method has the advantage of enabling the microscopist to observe the differences in hardness between microscopical areas of different constituents in the same resin.



FIGURE 5. RUBBER TIRE STOCK ( $\times 5$ )  
Stretched twice its length, orthogonal light. Normal behavior of accelerator

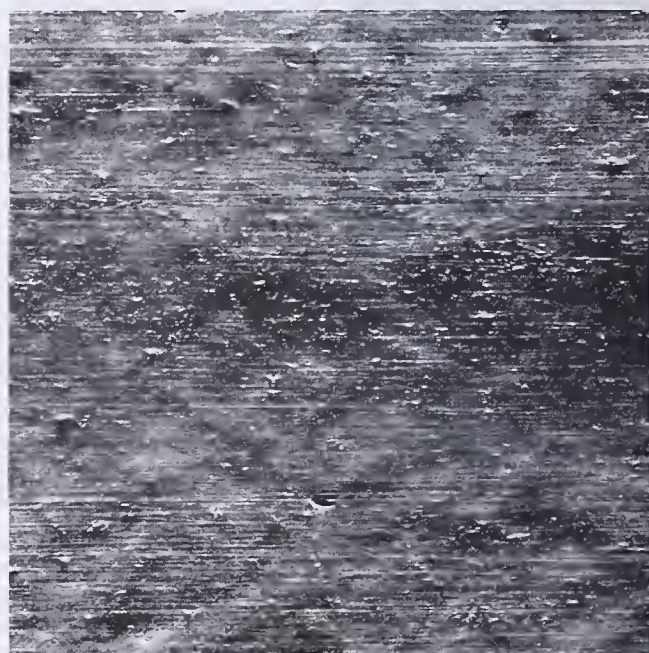


FIGURE 6. RUBBER TIRE STOCK ( $\times 5$ )  
Stretched twice its length, orthogonal light. Localized, over-active accelerator



The refractive indices, specific gravity, and Brinell hardness of some common resins are shown in Table I.

In addition to the above-mentioned properties, such specific temperatures as the points of melting, softening, sublimation, or decomposition, may be determined on the hot stage of the microscope. Solubility in determinative solvents may also be observed. The microscope has proved to be a valuable accessory lately in such physical tests as electrical breakdown potential, ultraviolet radiation effects, temperatures of scorching, and variations in humidity.

Microscopical qualitative analyses may be made on the original resin, its decomposition products, its separable fillers, or its impurities. A similar chemical analysis of the ignited ash usually serves to identify the inorganic pigments and the inorganic bases of organic lakes.

Petrographic analyses serve to identify fragments of minerals and synthetic chemicals in natural resins. Microscopical

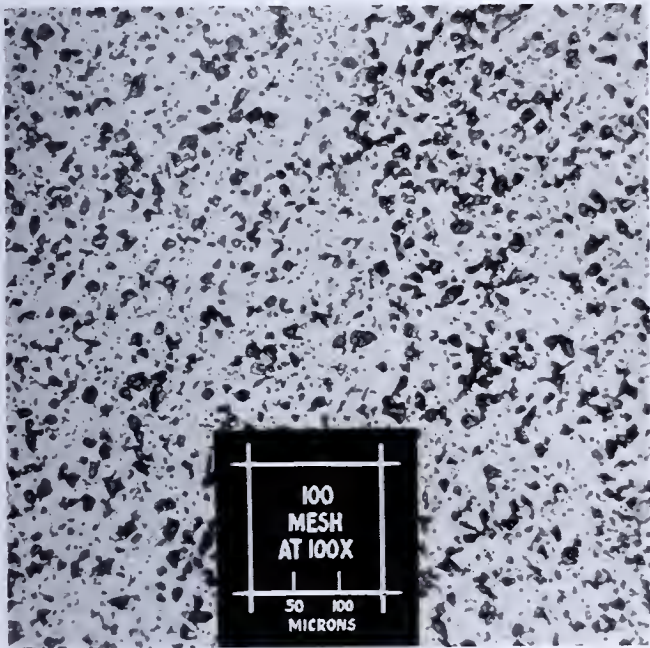


FIGURE 7. COMMERCIAL GROUND RUBBER SULFUR (× 100)

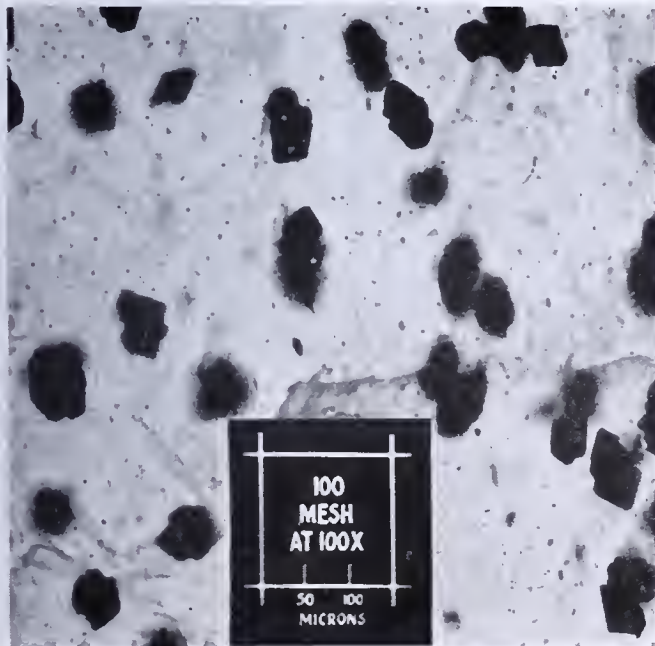


FIGURE 8. THIN SECTION OF MILLED UNVULCANIZED RUBBER, CONTAINING 3 PER CENT OF SULFUR (× 100)



FIGURE 9. THIN SECTION OF UREA-FORMALDEHYDE RESIN BETWEEN CROSSED NICOLS (× 100)

characteristics indicate the presence of portions of insects and vegetable fibers in such resins.

Microscopical Characteristics of Resin

The amorphous nature of a resin is characteristic, but occasionally, under certain conditions, a crystalline phase makes its appearance.

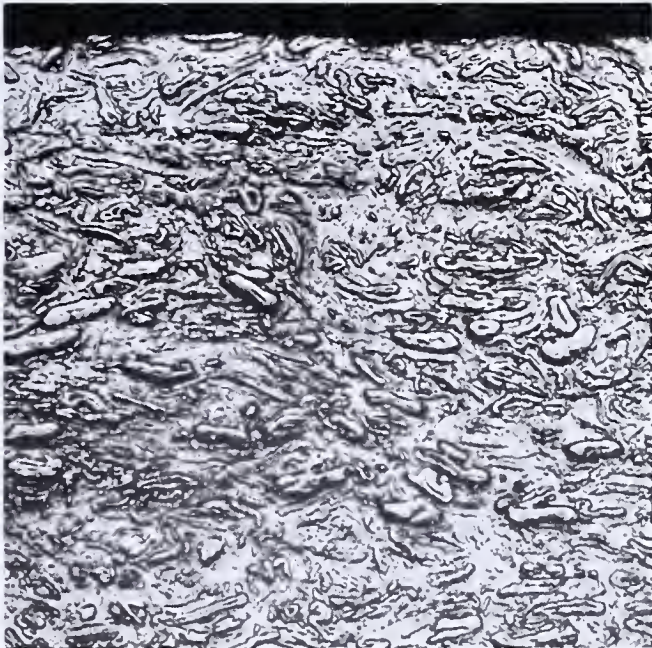


FIGURE 10. UREA RESIN WITH PAPER PULP FILLER (× 250)  
Polished cross section, showing normal distribution of fibers

The examination of resins under the microscope is also useful for the explanation of turbidity and opacity, in spots or throughout the resin. These phenomena are usually caused by tiny gas bubbles, pigment particles, impurities, microscopic crystals, nonplastic resin, or decomposition products.

The microscope is also a handy tool in the study of textile and brush fibers made from synthetic or semisynthetic resins



like the cellulose esters, regenerated cellulose, casein-formaldehyde, other coagulated proteins, vinyl resins, and glass. The microscopical examination of these fibers is not only extremely important in their identification, but also in the explanation of certain special properties such as delustering, curl, and crimp. Figure 1 shows the microscopical appearance of an artificial wool. By its original appearance, its behavior in reagents under the microscope, and a few organic qualitative analyses, it was identified 5 years ago as casein-formaldehyde.

Resins are also used as adhesives, binders, and stiffening agents, as in laminating wood, cloth, and paper, and making sheets of ground cork. Figure 2 shows a cross section of

laminated paper, re-enforced on both sides (edges) with sulfur, a good, but relatively uncommon, resin.

The use of resins as surface coatings is a very extensive field in itself. They are used in paints, varnishes, lacquers, and printing inks, and as finishes for both papers and fabrics. The microscopical work includes the examination of the resin surface before and after it has undergone various empirical and practical tests. Space does not permit a more thorough discussion of this important field, but it is interesting to note the microscopical appearance of the erosion spots on a test panel after exposure in the Weatherometer, as shown in Figure 3. Microscopic cracks which developed, upon exposure in the Weatherometer, on a very brittle enamel film are shown in Figure 4.

The stresses and strains in brushed, dipped, and sprayed



FIGURE 11. PHENOLIC RESIN WITH PAPER PULP FILLER ( $\times 250$ )

Polished cross section, showing extreme segregation of fibers



FIGURE 13. PHENOLIC RESIN WITH WOOD FLOUR AS FILLER, POLISHED CROSS SECTION ( $\times 250$ )

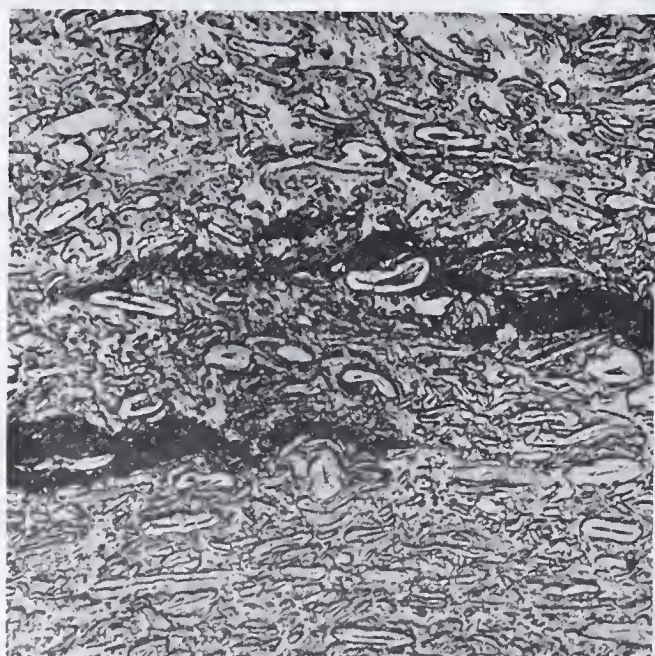


FIGURE 12. UREA RESIN WITH PAPER PULP FILLER ( $\times 250$ )

Polished cross section, illustrating effect of heat on molded piece



FIGURE 14. PHENOLIC RESIN WITH GROUND WOOD AND MINERAL FILLERS POLISHED CROSS SECTION ( $\times 250$ )



films and cast and molded forms are all distinguishable with polarized light, especially under the microscope.

An article by Weigel (6) came to hand after the preparation of this manuscript. It is heartily recommended to the microscopical investigator of synthetic molded resins. The author relies chiefly on stains to differentiate fillers from the resin.

The surface of a fabricated resin may often indicate phenomena which have taken place within it. Figure 5 shows the surface of a piece of rubber tire stock with a normal appearance after stretching to twice its original length (1). Figure 6 shows another sample pictured under identical conditions but containing segregated particles of an accelerator whose action was so rapid that it cured certain small areas of the rubber below the curing temperatures, with the result that, after curing, these areas were not so elastic as their

matrix, and they appeared as tiny bumps when the piece was stretched.

Internal Structure of Molded Resins

THIN SECTIONS. Sometimes the internal structure of a resin may be shown microscopically in transmitted light by cutting a cross section sufficiently thin. For comparison with the next photomicrograph, Figure 7 shows a sample of commercial, ground rubber sulfur, as received. Figure 8, under the same magnification, shows a microtomed section of milled rubber, before vulcanization, containing 3 per cent of the same sulfur. This photomicrograph shows that a few of the sulfur particles have grown into large crystals or clusters of crystals, with free rhombic faces, at the expense of other particles.

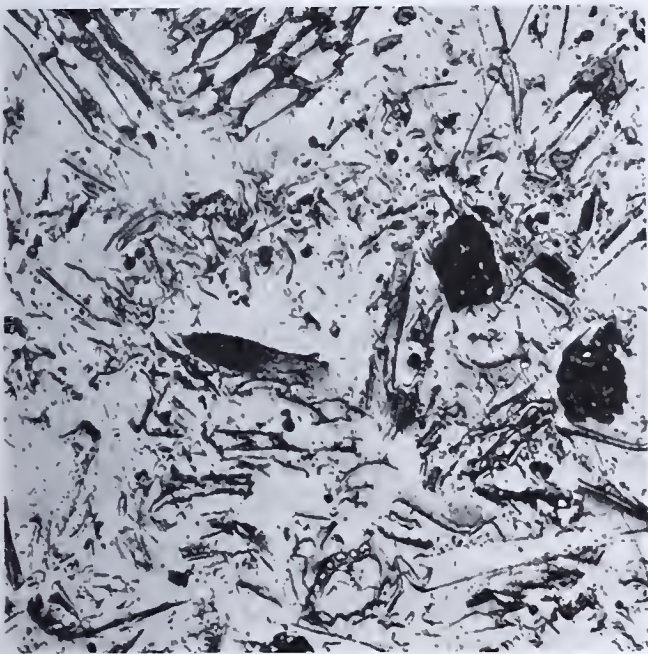


FIGURE 15. HEMP HURDS IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (X 250)



FIGURE 17. SUGAR CANE IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (X 250)

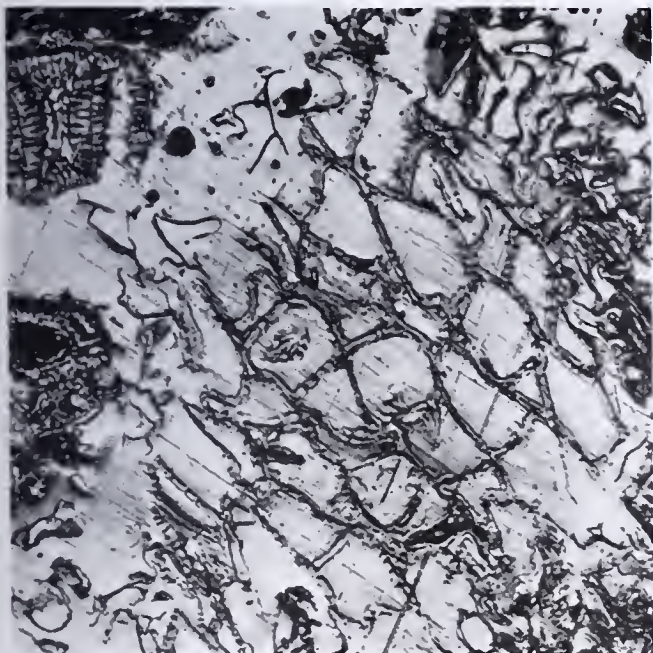


FIGURE 16. CORK IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (X 250)

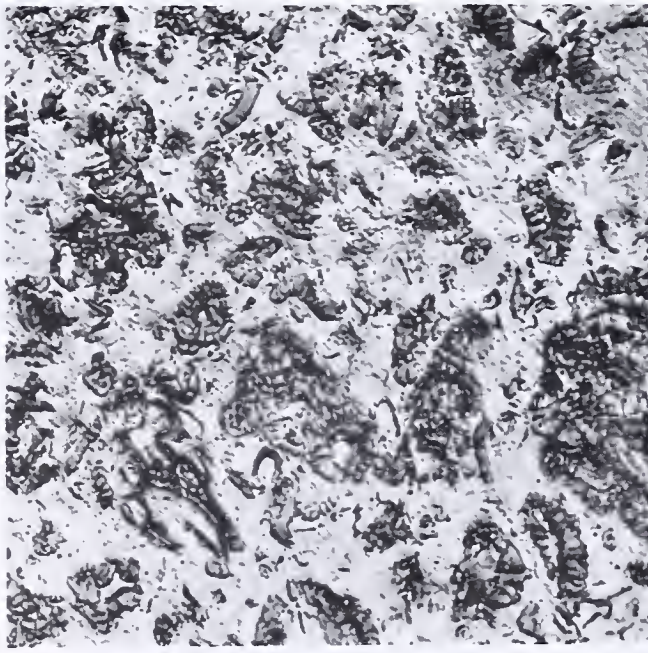


FIGURE 18. WALNUT SHELLS IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION (X 250)



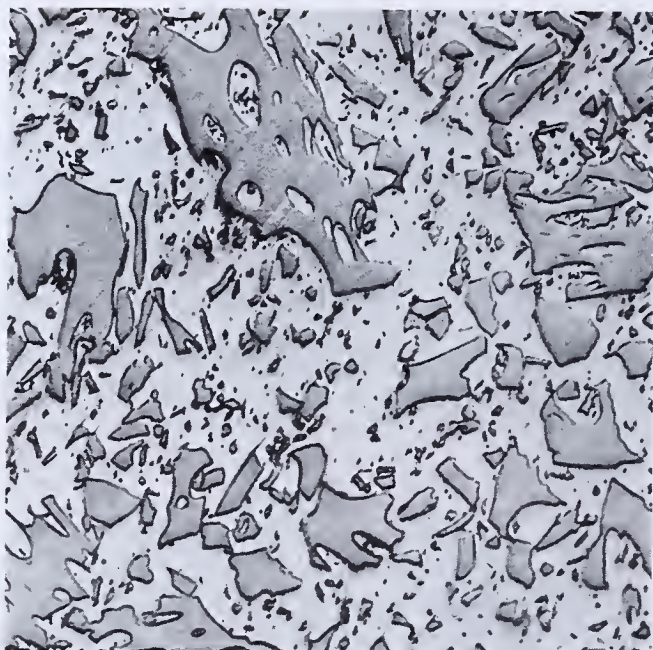


FIGURE 19. PUMICE IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION ( $\times 250$ )

Sometimes a thin section may be ground mechanically from a molded resin. Figure 9 shows a ground thin section of a urea-formaldehyde resin, between crossed Nicols, to show the fibers of alpha-cellulose pulp. Recently, the author has found that the shaving removed from a urea-formaldehyde molding, by turning it on a lathe, is very satisfactory for microscopical examination. A shaving of ample length can easily be made with a uniform thickness of 0.025 mm. (0.001 inch, or 25  $\mu$ ).

**POLISHED CROSS SECTION.** The examination of opaque molded resins is usually done more quickly and easily in polished cross section than in thin section. (Details for preparing and examining polished cross sections of molded and laminated resins are to be published later.) In addition, a polished section is easier to prepare in a specially oriented section, such as a cross section through the molded surface.

Figure 10 illustrates the microscopical appearance of a cross section of a molded urea-formaldehyde resin containing chemically prepared paper pulp. The section is perpendicular to the molded surface, and the upper edge of the section represents the molded edge. Notice the shortness of the discrete paper fibers and the uniformity of their distribution, even out to the molded edge.

Figure 11 shows an example of extreme segregation of the paper fibers. The molded edge of the fiber-free area lies in a spotted area on the molded surface.

The area shown in Figure 12 is a portion of a molded piece of urea resin which had been used in measuring the elevated temperatures at which the resin became opaque and finally brown. Notice that the resin has darkened in places and that cracks originate in these areas and continue between the fibers.

**OTHER VEGETABLE FILLERS.** The distribution of the fibers of ground wood in molded resin is illustrated in Figures 13 and 14. Figure 13 shows that some of the fiber bundles are relatively large. They are shown in longitudinal, diagonal, and transverse sections. Near the molded edge, the fibers are relatively small and, in some places, scarce.

In Figure 14, the fibers are smaller and much more uniformly distributed. The fibers are usually oriented parallel to the molded edge. The photomicrograph also serves to point out the presence of particles of mineral filler.

The next four photomicrographs show the microscopical appearance in polished cross section of molded resin containing

some less common fibers which might be encountered in analytical work. Figures 15 through 18 are photomicrographs, respectively, of hemp "hurds" (hemp pith), cork, sugar cane, and walnut shells, each molded in a phenolic resin.

**MINERAL FILLERS.** Some mineral fillers may be identified by their microscopical structure by means of light vertically reflected from a polished cross section, even though the minerals are usually classified as transparent (poor reflectors).

Figure 19 illustrates the peripheral and internal structure of cross sections of pumice particles. The presence of internal voids and the curved indentations in the outline of the fragments would serve to identify the filler quickly.

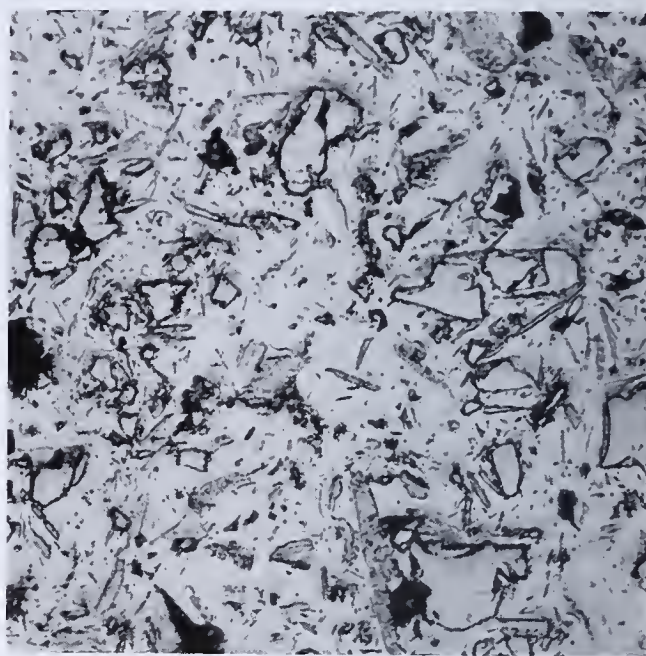


FIGURE 20. TALC IN MOLDED PHENOLIC RESIN, POLISHED CROSS SECTION ( $\times 250$ )

In Figure 20, some of the particles appear fragmental but others are thin and elongated (almost fibrous). These latter may be edge views of flaky particles or they may be actually fibrous. The elongated views are characteristic of certain varieties of talc minerals.

### Acknowledgment

The author is indebted to his colleagues, R. L. Gilbert, R. W. Stafford, and L. Boor, for their aid in the collection of these data, and to C. W. Mason and E. G. Rochow for their very helpful advice in the preparation of the manuscript.

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# A Semimicro-Kjeldahl Distillation Apparatus

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NUMEROUS designs have been published for both macro- and micro-Kjeldahl distillation units. Some of these are very satisfactory in their performance, but all show some tendency to suck back the standard acid unless considerable care is exercised by the operator. A few require for fabrication a degree of skill in glass blowing seldom attained by anyone other than a professional glassblower. Various sources of error in both the macro- and micro-Kjeldahl determination of nitrogen have been discussed by Schulek and Vastagh (2). The use of rubber connections, to which these authors strongly object, is less objectionable than was formerly the case because of the high grade of amber-colored pure gum tubing and stoppers now available, and the small area of rubber in contact with the steam which suitable design readily reduces to less than 1 sq. cm. The loss in ammonia resulting from the large volume of air diluting the ammonia in the early part of the usual Kjeldahl distillation, to which Miller (1) has called attention, is best prevented by sweeping out the air in the apparatus with steam before liberating the ammonia with alkali.

The semimicro-Kjeldahl distillation unit herein described possesses the following advantages: Distillation is carried out from the same flask in which the digestion is performed, which in this case is a standard 100-ml. Pyrex Kjeldahl

distillation flask. No ammonia is liberated until all the air has been swept out of the apparatus with steam. None of the standard acid in the receiver is sucked back into the distillation flask. The entire apparatus may be assembled on a single small-sized ring stand, thus making the unit both rigid and easily portable. A large number of determinations can be made with a single piece of apparatus in a short time, since cleaning is extremely rapid and distillation of the ammonia requires only a few minutes. In addition, the apparatus is built in three closely coupled units, any one of which may be easily removed for repair in the event of breakage.

## Construction

The construction of the apparatus is adequately explained by Figure 1.

The capillary tip below the stopcock should have a bore between 2 and 3 mm. If the bore is smaller than 2 mm. the sodium hydroxide runs in too slowly, while if the bore is much larger than 3 mm. a solid column of liquid fails to form and steam may be expelled through the funnel top above the stopcock. The inner tube in the condenser must be of thin-walled glass to give adequate heat transfer.

The small trap on the filler tube in the steam-generating flask prevents water from spurting out of it during distillation, at the same time leaving the flask open to atmospheric pressure.

As a consequence, if the standard acid starts to suck back out of the receiver, it rises only a few centimeters in the delivery tube before a few bubbles of air are drawn through the filler tube into the apparatus. These bubbles having restored atmospheric pressure within the apparatus, the distillation then continues without interruption. Water may also be run into the flask without removing the filler tube from the apparatus. The tube below the small trap in the filler tube should be at least 25 cm. in length and should extend nearly to the bottom of the large flask. The style of trap used here has been found very efficient and is desirably compact.

## Operation

A 20- to 60-mg. sample is weighed into a 100-ml. Pyrex Kjeldahl distilling flask, and 2 to 5 ml. of c. p. concentrated sulfuric acid and any one of the numerous catalysts that have been suggested are added, the selenium-mercury-potassium sulfate mixture (3) being one of the best. Digestion is then completed in the usual manner. The flask and contents are allowed to cool to room temperature, after which 15 to 20 ml. of distilled water are added and the contents of the flask are well mixed. During the digestion of the sample the large flask in the distillation unit is filled approximately two-thirds full of distilled water and heated to boiling with an efficient burner. A blank Kjeldahl flask is fitted in place and the apparatus is well steamed. The blank Kjeldahl flask is now removed and replaced by one containing the diluted digested sample. A second burner is placed under the Kjeldahl flask and the two burners are so regulated that a moderate current of steam passes into the Kjeldahl flask. In the meantime a 200-ml. conical flask containing an appropriate amount of standard acid is placed under the delivery tube with the tip of the delivery tube about 1 cm. below the surface of the acid.

After the apparatus is completely filled with steam, the burner is temporarily removed from under the Kjeldahl flask and 10 to 15 ml. of 18 N sodium hydroxide solution, which has been allowed to stand until carbonate-free, are added in

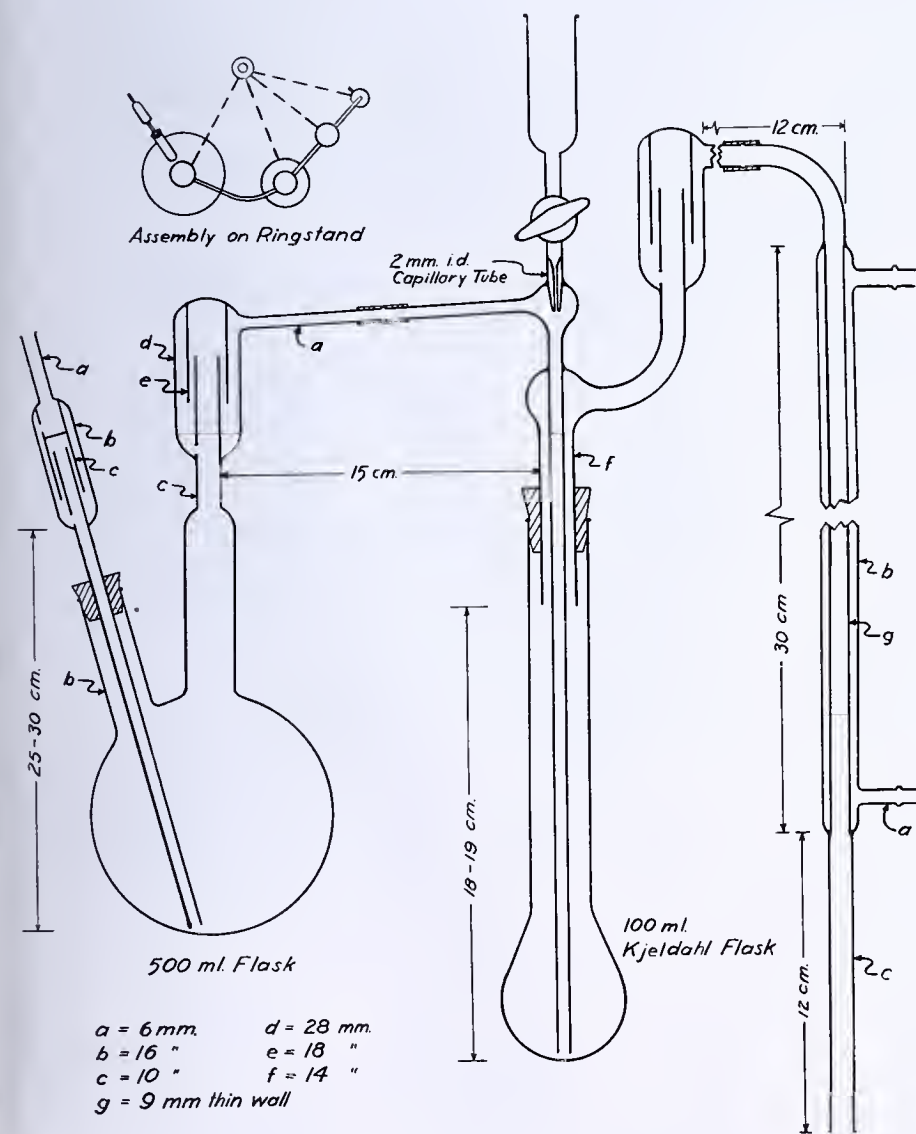


FIGURE 1. APPARATUS



TABLE I. TEST RUNS ON KJELDAHL DISTILLATION APPARATUS

Time of Distillation Min.	Nitrogen Found Mg.	Nitrogen Present Mg.	Error %	Deviation from Mean of Group %
8	12.47	12.42	+0.4	+0.2
8	12.43	...	+0.08	-0.08
7	12.42	...	0.00	-0.16
7	12.42	...	0.00	-0.16
6	12.43	...	+0.08	-0.08
6	12.47	...	+0.4	+0.2
6	3.094	3.110	-0.5	-0.2
6	3.107	...	-0.1	+0.1
6	3.104	...	-0.2	-0.06
6	0.627	0.625	+0.3	0.0
6	0.629	...	+0.6	+0.3
6	0.627	...	+0.3	0.0
6	0.624	...	-0.2	-0.5

the course of 1 to 2 minutes, slowly enough to avoid excessive heating. (If a mercury catalyst has been used 1 to 2 ml. of 1 *M* sodium sulfide solution should be added immediately after the sodium hydroxide.) The burner is then replaced under the Kjeldahl flask and the two burners are so adjusted that 40 to 50 ml. of distillate collect in 10 to 12 minutes. If bumping starts, the burner under the Kjeldahl flask is turned out and the other one is increased. After 8 to 10 minutes the receiver is lowered and 5 to 10 ml. of additional distillate are collected, the lower end of the condenser being above the surface of the solution in the flask. The acid in the receiver is then titrated in the usual manner.

### Performance

To test the performance of the apparatus a standard solution of ammonium sulfate was used, so that no error due to incomplete digestion would be introduced. The data in

Table I show the excellent performance of this apparatus, even with much shorter periods of distillation than those recommended and with samples containing as little as 0.6 mg. of nitrogen in the form of ammonium sulfate. This series of determinations represents a complete group of test distillations. No results were omitted because of inaccuracy. To make sure that the standard acid could not be sucked back, in several determinations the burners were turned off while the apparatus was in the midst of a distillation. No sucking back occurred in any part of the apparatus.

### Summary

Directions are given for constructing and operating a semi-micro-Kjeldahl distillation apparatus embodying the following advantages: one flask only for digestion and distillation; standard acid not subject to sucking back; apparatus compact and portable; and ammonia not liberated until apparatus is air-free.

The precision on samples containing as little as 0.6 mg. of nitrogen indicates that this apparatus may be used even on a micro scale.

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CONTRIBUTION 719, California Institute of Technology.

## Constant-Level Still for Redistillation of Water

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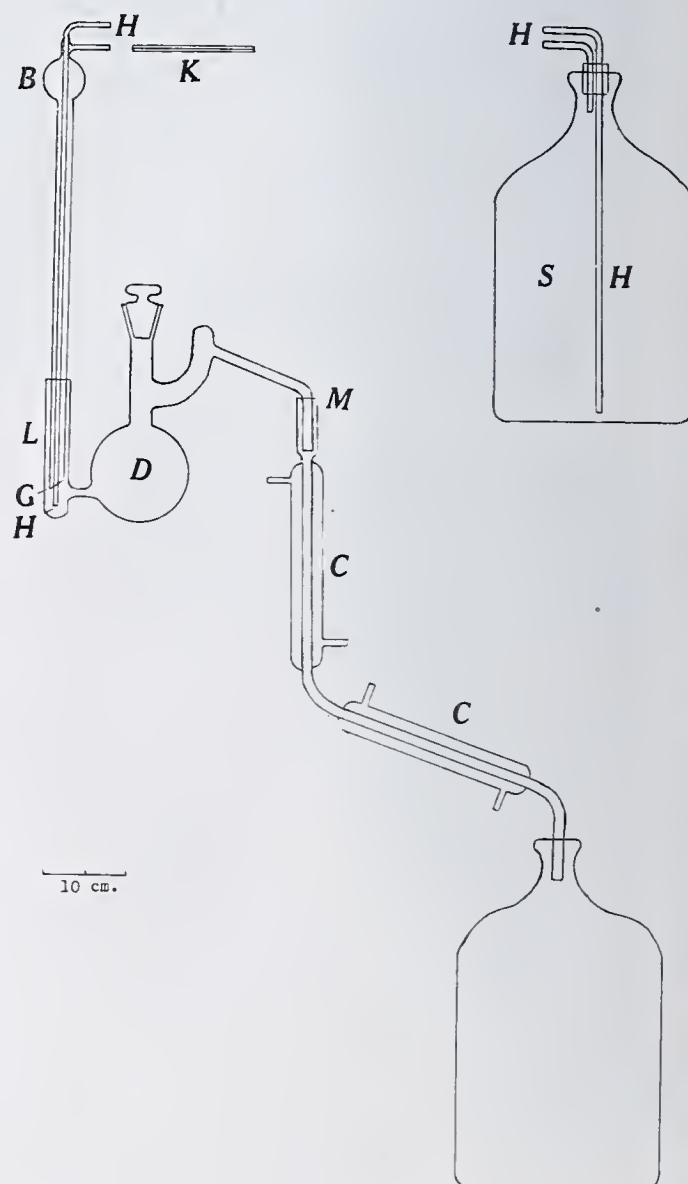
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**I**N METHODS for the determination of microgram quantities of various elements, such as iodine or lead, water redistilled from alkali or alkaline permanganate must be routinely used for the final washing of all glassware. Of the various setups that have been tried over a period of 3 years in this laboratory for the continuous redistillation of water, the one described here is the best. It has also been used successfully in two other laboratories in this district.

The figure is drawn to scale, as indicated. Water is boiled in a modified 1-liter Claisen flask, *D*, with two or three beads to prevent bumping, and is condensed in the double condenser, *C, C*. When the level of water in *D* drops below any point predetermined by the height to which *G* is set, air passes up through the water in the outer column to the safety bulb, *B*, and thence through the capillary, *K*, to the reservoir bottle, *S*. This starts the flow of water through the siphon tube, *H*. The flow continues until the end of *G* is again covered with water and the water in *G* is in hydrostatic equilibrium with that in reservoir *S*. The purpose of capillary *K* is to introduce an appreciable lag in the flow of water into flask *D*, so that in no case does the water cease boiling. The condenser bore must not be appreciably smaller than the outlet, *M*. Thus, with a coil-type condenser the constant-level device did not function. Although any condenser meeting the above requirement may be used, the compact double condenser, *C, C*, is found to give adequate condensation.

To keep out dust, it is well to cover *L* with Pyrex glass wool. *M* may be closed entirely.

The apparatus may be mounted by using a rod frame against a laboratory shelf on which *S* sits, or by constructing a wooden stand.





# INDUSTRIAL and ENGINEERING CHEMISTRY

ANALYTICAL EDITION



Harrison E. Howe, Editor

## Determination of Iodine

### In Thyroid and Its Preparations by Cerate Oxidimetry

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IN AN attempt to develop a procedure which would be superior to that in the U. S. Pharmacopœia XI for the determination of iodine in thyroid preparations, the methods presented in the literature by Middleton (4), Kendall (2), and Harrington and Randall (1), involving fusion with an alkali in the presence of an oxidizing agent, and by Trevorow and Fashena (7), incorporating oxidation in an acid medium, were investigated.

In the former methods the solutions of the fusion mass are neutralized and made acid, after which an excess of either chlorine or bromine is added for the purpose of oxidizing any iodide to the iodate form. In the authors' opinion, inconsistent results, obtained by these methods, are due to technical difficulties in eliminating these excess oxidizing agents. The latter method proved to be unsatisfactory for routine analysis.

Further search of the literature revealed the more recent works of Lewis (3) on the determination of iodides by ceric sulfate and of Smith (5, 6) on the volumetric oxidation by ceric sulfate and the application of *o*-phenanthroline as an indicator in this reaction.

#### Experimental

The authors' recent experimental work reveals that when thyroid gland or a mixture of thyroid gland and a diluent is fused with anhydrous sodium carbonate both inorganic and organic iodine combines with sodium to form sodium iodide. Since this iodide salt and the unused sodium carbonate are readily soluble in water, the insoluble carbonaceous material can be removed by filtration. The resulting solution, when acidified with hydrochloric acid to make a 2 *M* (molar) solution of the acid, can be titrated with volumetric ceric sulfate and the percentage of iodine contained in the original thyroid sample calculated.

The sodium iodide formed in the reaction described above is quantitatively oxidized by the ceric sulfate solution according to the following equation:



#### Reagents

ANHYDROUS SODIUM CARBONATE, reagent grade.

CERIC SULFATE SOLUTION, 0.005 *N*. Dissolve 1.70 to 1.80 grams of anhydrous ceric sulfate [ $\text{Ce}(\text{SO}_4)_2$ , molecular weight 332.25] in 1000 cc. of cold, dilute sulfuric acid made by adding 300 cc. of dilute sulfuric acid (one volume of water plus one volume of concentrated sulfuric acid) to 700 cc. of water. The salt

first hydrates and with continued stirring in the cold completely dissolves and is ready to be standardized as follows:

Transfer 2 cc. of standardized ferrous sulfate solution to a 250-cc. beaker, using a calibrated pipet, and dilute to 100 cc. with 2 *M* sulfuric acid or hydrochloric acid. Add 1 drop of 0.025 *M* *o*-phenanthroline ferrous complex and titrate with the unknown ceric sulfate solution. The end point is from pink to pale green. An overstepped end point can be back-titrated (color change, slightly green to pink).

$$\text{Normality of Ce}(\text{SO}_4)_2 = \frac{\text{volume of 0.1 N FeSO}_4 \times 20}{\text{volume of Ce}(\text{SO}_4)_2 \text{ required}} \times \text{normality of FeSO}_4$$

This solution has been found to remain stable for periods of at least 2 months.

FERROUS SULFATE, 0.1 *N*. Dissolve 27.80 grams of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) in 980 cc. of water to which have been added 20 cc. of dilute sulfuric acid (one volume of concentrated sulfuric acid plus one volume of water). Standardize as follows:

Take 25- or 50-cc. portions of the approximately 0.1 *N* solution of ferrous sulfate with a calibrated pipet and transfer to a 250-cc. beaker. Dilute to 200 cc. with 2 *M* sulfuric or hydrochloric acid. Add 1 drop of 0.025 *M* *o*-phenanthroline ferrous complex and titrate with standard potassium dichromate until the pink solution turns pale green. An overstepped end point can be back-titrated (color change, pale green to pink).

$$\text{Normality of FeSO}_4 = \frac{\text{volume of 0.1 N K}_2\text{Cr}_2\text{O}_7 \text{ required}}{\text{volume of FeSO}_4 \text{ required}} \times 0.1$$

POTASSIUM DICHROMATE, 0.1 *N*. Dissolve 4.9035 grams of reagent potassium dichromate, which has been pulverized and dried to constant weight at 120° C., in sufficient distilled water to measure exactly 1000 cc. at standard temperature.

*o*-PHENANTHROLINE FERROUS SULFATE SOLUTION, 0.025 *M*. *o*-Phenanthroline monohydrate, molecular weight 198, melting point 90–100° C. Use 1.485 grams for 100 cc. of 0.025 *M* solution as below. Ferrous sulfate, 0.025 *M* solution. Use 0.695 gram of ferrous sulfate heptahydrate in 100 cc. of solution. Make fresh as needed.

Dissolve the ferrous sulfate, add the *o*-phenanthroline monohydrate, and stir until all is dissolved, giving a dark red solution. One drop of this indicator serves for each titration in a volume of approximately 150 cc.

HYDROCHLORIC ACID, reagent grade.

#### Procedure for Thyroid Gland

Thoroughly mix 1 gram of thyroid, finely powdered and accurately weighed, with 15 grams of anhydrous sodium carbonate in a nickel crucible of about 125-cc. capacity, and spread an additional 10 grams of anhydrous sodium carbonate evenly over the surface. Heat the crucible in the flame of a Bunsen burner at a rate to attain a dull red color in 10 minutes. Then place the crucible and contents in a muffle furnace and heat at a temperature not to exceed 500° C. for 30 minutes. Cool the mixture and transfer it to a 250-cc. beaker containing 100 cc. of warm distilled water. Rinse the crucible with 25 cc. of dis-



tilled water and add it to the beaker. Apply gentle heat to the beaker and contents to ensure solution of the sodium carbonate and iodide. Filter the solution while still warm and wash the carbonaceous material with several small portions of warm distilled water.

Cool the filtrate and cautiously neutralize with concentrated hydrochloric acid, using litmus paper as an indicator. For each 100 cc. of neutralized solution, add 20 cc. of concentrated hydrochloric acid and titrate with 0.005 *N* ceric sulfate, using a micro-

buret and 1 drop of *o*-phenanthroline ferrous sulfate, 0.025 *M* solution, as indicator, the end point being the first bluish green tinge that remains in the solution for 1 minute. Conduct a blank test with the same quantities of the same reagents omitting only the thyroid, and fusing as directed, and subtract the volume of 0.005 *N* ceric sulfate consumed from that consumed by the thyroid.

Each cubic centimeter of 0.005 *N* ceric sulfate is equivalent to 0.0003178 gram of iodine in thyroid combination.

TABLE I. COMPARISON OF RESULTS FOR THYROID GLAND

(Weight of sample, 1.0000 gram)				
Assay Method	Sample	0.005 <i>N</i> Ce(SO <sub>4</sub> ) <sub>2</sub>	0.005 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	Iodine
		Required <sup>a</sup>	Required <sup>a</sup>	
		<i>Cc.</i>	<i>Cc.</i>	%
Proposed	A	6.132	...	0.1949
	A	6.151	...	0.1955
	A	6.403	...	0.2035
	A	6.203	...	0.1971
	A	6.353	...	0.2019
U. S. P. XI	A	...	20.22	0.214
	A	...	21.50	0.228
Proposed	B	5.953	...	0.1892
	B	5.903	...	0.1876
	B	5.953	...	0.1892
	B	5.733	...	0.1822
	B	5.653	...	0.1797
U. S. P. XI	B	...	21.26	0.225
	B	...	20.04	0.212

<sup>a</sup> Blank previously deducted.

TABLE II. COMPARISON OF RESULTS FOR 6.48-MG. (0.1-GRAIN) THYROID TABLETS

Assay Method	Thyroid in Sample Grains	0.005 <i>N</i> Ce(SO <sub>4</sub> ) <sub>2</sub> Required <sup>a</sup> Cc.	0.005 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Required <sup>a</sup> Cc.	Iodine per Tablet Mg.	Per Cent of Labeled Amount of Thyroid
Proposed	4.00	1.649	...	0.001310	100.46
	4.00	1.667	...	0.001324	101.56
	4.00	1.722	...	0.001368	104.90
	4.00	1.740	...	0.001382	106.00
	4.00	1.676	...	0.001332	102.10
	4.00	1.640	...	0.001303	99.91
U. S. P. XI	2.50	...	2.300	0.000973	75.10
	2.50	...	2.600	0.001100	84.90

<sup>a</sup> Blank previously deducted.

TABLE III. COMPARISON OF RESULTS ON MANUFACTURERS' SAMPLES OF 64.8-MG. (1-GRAIN) THYROID TABLETS

Assay Method	Sample	Thyroid in Sample Grains	0.005 <i>N</i> Ce(SO <sub>4</sub> ) <sub>2</sub> Required <sup>a</sup> Cc.	0.005 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Required <sup>a</sup> Cc.	Iodine per Tablet Mg.	Per Cent of Labeled Amount of Thyroid
Proposed	A	10	4.149	...	0.01319	101.74
	A	10	4.240	...	0.01348	102.95
	A	10	4.348	...	0.01382	106.62
	A	10	4.155	...	0.01321	101.79
	A	10	4.043	...	0.01285	99.14
	A	10	3.983	...	0.01266	97.67
U. S. P. XI	A	12	...	14.80	0.01305	100.70
	A	12	...	16.00	0.01411	108.80
	A	12	...	14.58	0.01285	99.19
Proposed	B	10	4.092	...	0.01300	100.34
	B	10	4.072	...	0.01294	99.85
	B	10	4.131	...	0.01313	101.30
	B	10	4.102	...	0.01303	100.59
	B	10	4.013	...	0.01275	98.40
	B	10	4.033	...	0.01282	98.89
U. S. P. XI	B	12	...	16.25	0.01433	110.50
	B	12	...	16.10	0.01420	109.50
Proposed	C	10	4.112	...	0.01307	100.83
	C	10	4.171	...	0.01326	102.28
	C	10	4.161	...	0.01322	102.13
	C	10	4.289	...	0.01363	105.17
	C	10	4.250	...	0.01351	104.22
	C	10	4.230	...	0.01344	103.73
U. S. P. XI	C	15	...	19.97	0.01409	108.60
	C	15	...	19.49	0.01375	106.10
Proposed	D	10	4.112	...	0.01307	100.83
	D	10	4.072	...	0.01294	99.85
	D	10	3.993	...	0.01269	97.91
	D	10	4.191	...	0.01332	102.77
	D	10	4.103	...	0.01304	100.61
U. S. P. XI	D	12.72	...	17.59	0.01463	112.10
	D	12.72	...	18.22	0.01515	116.90

<sup>a</sup> Blank previously deducted.

Procedure for Thyroid Tablets

Weigh not less than 20 of the tablets and reduce them to a fine powder without an appreciable loss. Substitute approximately 1 gram of tablet mixture, accurately weighed, for the thyroid sample and proceed with the proposed and U. S. P. XI methods for the assay of thyroid gland. The sample weight should be increased so that the amount of thyroid will equal or exceed 259.2 mg. (4 grains).

Percentages of the labeled amount found are calculated on the basis of 0.200 per cent iodine in the thyroid gland.

Accuracy of Method

A mixture consisting of four parts of potassium iodide (99.40 per cent KI) and one part of lactose, having a theoretical iodine content of 60.78 per cent, was assayed by both the U. S. P. XI and the proposed methods for thyroid. Results obtained are listed in Table V.

Comments and Conclusions

Fusion of the thyroid material with anhydrous sodium carbonate does not destroy the carbonaceous material. However, this does not interfere with the solubility of the sodium iodide formed in the reaction. Attempts to incorporate an oxidizing agent with the anhydrous sodium carbonate to destroy the carbonaceous material proved unsatisfactory, in that it interfered with the ceric sulfate titration.

The sodium chloride formed when the excess sodium carbonate is neutralized with hydrochloric acid does not interfere with the oxidation of the sodium iodide. Sulfuric and nitric acids, if used to neutralize the excess sodium carbonate, give salts which are easily oxidized by ceric sulfate and thus give high results.

The data as listed in the tables show the comparable results that may be obtained by the two methods. The proposed method has the advantage of titrating the original iodide formed in the fusion reaction and thus does not introduce any other steps which are likely to interfere with the final result. The proposed method is applicable for the gland as well as

TABLE IV. COMPARISON OF RESULTS FOR 129.6-MG. (2-GRAIN) THYROID TABLETS

Assay Method	Thyroid in Sample Grains	0.005 <i>N</i> Ce(SO <sub>4</sub> ) <sub>2</sub> Required <sup>a</sup> Cc.	0.005 <i>N</i> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> Required <sup>a</sup> Cc.	Iodine per Tablet Mg.	Per Cent of Labeled Amount of Thyroid
Proposed	10	3.894	...	0.02475	95.49
	10	3.954	...	0.02513	96.96
	10	3.875	...	0.02463	95.02
	10	3.865	...	0.02457	94.77
	10	3.944	...	0.02507	96.71
	10	3.993	...	0.02538	97.91
U. S. P. XI	20	...	23.20	0.02455	94.70
	20	...	23.00	0.02433	93.88

<sup>a</sup> Blank previously deducted.

TABLE V. ACCURACY OF METHOD

Method	Weight of Sample Gram	Iodine %	Deviation from Theory %
Proposed	0.1000	60.84	+0.06
	0.1000	60.84	+0.06
	0.1000	60.63	-0.15
	0.1000	60.56	-0.22
U. S. P. XI thyroid	0.1000	62.37	+1.59
	0.1000	62.17	+1.39



tablets of all grainages of thyroid, whereas, the authors know of no other method which gives accurate and consistent results with thyroid tablets.

The proposed method may be modified to make it applicable for the determination of thyroxine in the thyroid gland and its preparations.

#### Acknowledgments

The writers wish to express their sincere appreciation to Edward J. Hughes and Robert M. Lingle for their assistance in the preparation of this paper.

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## A Photelometric Study of the Lead-Dithizone System at 610 Millimicrons

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IN ADAPTING the Photelometer (5) to the measurement of the lead-dithizone complex in chloroform for the quantitative determination of lead, various filters were tried with a 1-cm. absorption cell and a distilled water reference solution. In the preliminary work light filters transmitting in the vicinity of 510  $m\mu$  were used, following the suggestion of Clifford and Wichmann (3). In this spectral range the red lead complex absorbs strongly and the green dithizone transmits freely. Using the chemical procedure as outlined by the Association of Official Agricultural Chemists (1) for the mixed color method, appreciable spreads were obtained between 0 and 50 micrograms of standard lead solution. However, the small change in transmission for this lead range precluded its use as a routine method. Using the same chemical procedure, the spread was approximately doubled when a filter having a maximum transmission at 610  $m\mu$  was substituted for the blue-green filter. The transmission curves of the lead-dithizone system as shown by Clifford and Wichmann (2, Figure 1) indicate that such an increase in the spread is to be expected.

#### Experimental

Using the 610  $m\mu$  filter, a study was made to determine the relationship between the lead and dithizone-chloroform concentrations which would produce the greatest sensitivity for a given lead range. All reagents and apparatus were carefully purified, following the suggestions of the A. O. A. C. (1). Two batches of Eastman diphenylthiocarbazon (dithizone) were purified independently and were used to prepare two stock solutions of 30 mg. of dithizone per liter of redistilled c. p. chloroform. Solutions of 2, 4, 8, 12, and 16 mg. of purified dithizone per liter of redistilled chloroform were prepared by diluting the 30-mg. per liter stock solution. Two standard lead solutions (1 ml. = 1 microgram of lead) in 1 per cent nitric acid were prepared from two individual, twice-recrystallized batches of c. p. lead nitrate, using redistilled water from a Pyrex distillation apparatus. The ammonia-cyanide mixture was prepared by pouring a quantity of redistilled ammonia equivalent to 19.1 grams of ammonia into a 500-ml. volumetric flask, adding 100 ml. of a 10 per cent potassium cyanide solution, and diluting to the mark.

#### Procedure

The preparation of the standard lead solutions for color development was based on the method of the A. O. A. C. (1).

Twenty milliliters of the standard lead solution (1 ml. = 1 microgram) were pipetted into a 50-ml. volumetric flask and 1 per cent nitric acid was added to the mark. The resulting solution represented a 20-microgram lead standard in the proper condition for the color development. Standards ranging from

0 to 50 micrograms of lead were prepared by changing the quantity of the standard lead solution and diluting to the 50-ml. mark with 1 per cent nitric acid.

For color development the procedure was as follows: The 50-ml. aliquot containing the standard solution was poured into a 250-ml. Pyrex separatory funnel, 10 ml. of the ammonia-cyanide mixture were added from a buret, and from another buret 15 ml. of dithizone-chloroform solution (the concentration of dithizone depending on the lead range to be covered) were added. The separatory funnel was thoroughly shaken and the layers were allowed to separate. The chloroform layer was filtered and read immediately in the Photelometer. The water layer was discarded.

#### Discussion of Results

Five dithizone solutions were prepared by the above procedure and the calibration curves of Figure 1 were obtained. Each curve covers the range of solutions, the colors of which vary from green to red, and all curves are asymptotic to the vertical axis. The shapes of the curves, including curve E, are characteristic of the instrument when transmission increases with concentration (4). In general, for the filter photometer, actual transmission factors for low transmission values are usually too great. Furthermore, the vertical displacement in the substantially parallel portion of the curves corresponds to approximately 20 micrograms of lead for each change in the standard dithizone solution of 4 mg. per liter; 10 micrograms for a change of 2 mg. per liter.

The curves indicate that 15 ml. of a solution containing 12 mg. of dithizone per liter are appropriate for a lead range of 15 to 50 micrograms. For a lead range of 0 to 15 micrograms, 15 ml. of a solution containing 4 mg. of dithizone per liter are preferred. The spread between 0 and 5 micrograms of lead in scale divisions is approximately ten times as great on curve A as on curve E. However, curve A is valuable only when it is definitely known that the lead concentration of the unknown does not exceed approximately 5 micrograms. For example, using 15 ml. of a solution containing 2 mg. of dithizone per liter, the transmission of solutions containing 10, 20, 30, etc., micrograms of lead would be essentially the same, owing to the asymptotic nature of the curve for transmission factors near unity. Such a condition suggests that if the approximate amount of lead is unknown, a preliminary test should be made using 15 ml. of a more concentrated dithizone solution for which a calibration curve has already been prepared. If the lead is found to be extremely low, a second aliquot of the unknown may be treated with a more dilute dithizone solution, so as to utilize the greater sensitivity of the curves toward the right in Figure 1.

For the range 0 to 50 micrograms of lead two curves are sufficient—namely, B and D. Curve B is appropriate for the



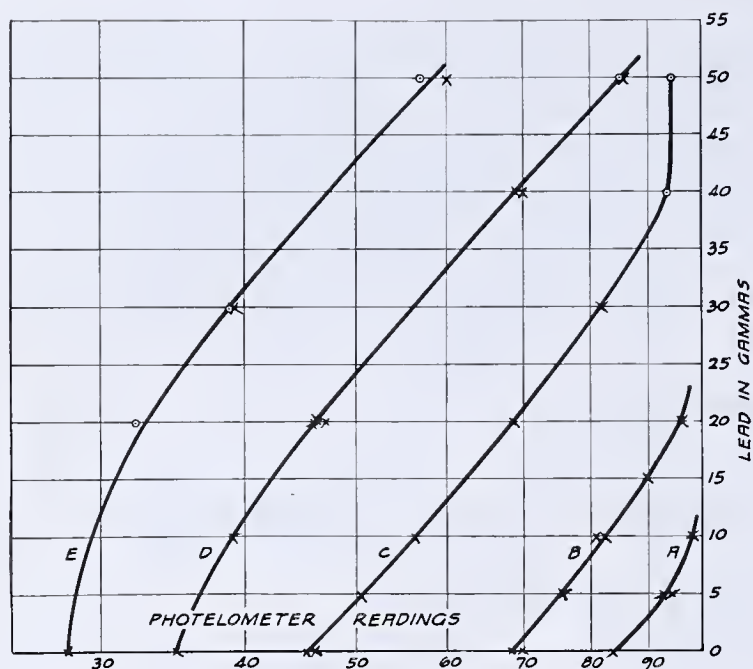


FIGURE 1. LEAD-DITHIZONE SYSTEM

The concentrations of dithizone for curves A, B, C, D, and E are 2.0, 4.0, 8.0, 12.0, and 16.0 mg. per liter, respectively. A different lead standard was used for each point; the circles and crosses indicate different dithizone solutions. Filter, 610  $m\mu$ , 1-cm. absorption cell. Volume of dithizone solution, 15 ml.

range from 0 to 15 micrograms and curve D is suitable for the region from 15 to 50 micrograms.

Although Clifford and Wichmann specify a blue-green filter for the lead-dithizone system, they make the following statement (3): "Theoretically a better spread could be obtained by working at 610  $m\mu$  but the mechanics of the reaction require a small excess of dithizone to be present even at the upper end of the range to hold the lead as  $PbD_2$  in the chloroform phase. Under these conditions the so-called 'saturated' color takes the form shown by the dotted line, the transmission being greatly repressed by this excess. Transmission in the green is little affected."

The importance of an excess of dithizone to prevent the decomposition of the red lead dithizone at the upper end of the lead ranges is recognized. However, the useful range of the calibration curves of Figure 1 obtains for solutions in which an excess of dithizone exists. The upper limit of the useful range of curve A corresponds approximately to a transmission factor of 0.97 (Photometer reading = 97.0); curve B, approximately 0.95; curve C, about 0.92; etc. Above these transmission factors where the excess of dithizone disappears because of its reaction with the greater quantities of lead, the decomposition of lead dithizone probably occurs on account of the equilibrium  $Pb + 2D \rightleftharpoons PbD_2$ . Thus, the instability of the complex lead dithizone occurs in the insensitive and unused portion of the calibration curve.

The precision of the instrument for the lead analysis may be determined from the curves of Figure 1. For the range of 0 to 15 micrograms of curve B, the readings cover twenty-two scale divisions which can be estimated within 0.2 division without difficulty and to 0.1 division by careful observers. This condition indicates a precision greater than 1 per cent. Thus, the precision of the instrument exceeds the accuracy of the chemical procedure even for this lower lead range.

Because of the possible instability of chloroform-dithizone solutions or the probable difficulty of preparing an exact duplicate of the original chloroform-dithizone solution, it is advisable to check each calibration curve frequently, using in the procedure a standard lead solution equivalent to the lead concentration at the lowest portion of the useful range of the curve. For curve D this standard solution would be a 15-

microgram lead standard, and for curve B a blank dithizone solution (15 ml. of a solution containing 4 mg. of dithizone per liter) would be appropriate. If the Photometer reading for these reference solutions deviates from the original calibration curves, all abscissas of the points on the curves should be displaced in the same direction an equal distance over the useful range of the curves. This shifting of the curves is legitimate as the useful portions of all curves are substantially parallel.

### Acknowledgment

The writer is indebted to members of the staff of this laboratory for their constructive criticisms.

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## A Method for Determining Deguelin in Derris and Cube

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WHEN derris or cube is extracted with a suitable solvent, such as chloroform, the resulting extractive can easily be divided into three fractions. The rotenone can be removed by crystallization from carbon tetrachloride (9, 10), and the remaining resin can be separated into an alkali-soluble and an alkali-insoluble portion (5). The last part has been assumed to consist largely of optically active deguelin, since racemic deguelin is often readily obtained on further treatment of this fraction with dilute alkali.

The insecticidal effect of the alkali insoluble fraction, which contains optically active deguelin, has been shown to be of the same order as that of rotenone (12). In its optically inactive form, however, deguelin and its dihydro derivative are much less toxic than rotenone, except when applied in kerosene-cyclohexanone solution (2, 12). Since the toxicity of the noncrystalline fraction may at times be due largely to the presence of optically active deguelin, a further study of the methods for determining this compound seemed desirable.

By subtracting that portion of the dehydro compound which results from rotenone, deguelin can be estimated by the method of Takei (13) or Tattersfield's modification (14), which depends on the formation of the dehydro compounds. Other materials similar to rotenone and deguelin would also be expected to form dehydro compounds, and the results by this method are probably too high. Cahn, Phipers, and Boam (1) report a method for the determination of deguelin that is based on the Goodhue modification (3) of the Gross and Smith red-color test. By this method they find the amount of deguelin in a given type of derris resin to be substantially constant. Recently the writers have encountered many samples which appear to have considerable deguelin when tested by both the red-color analysis and the dehydro-compound



method, but which give little or no crystalline material upon racemization with dilute alkali. This led them to suspect the presence of other compounds, and consequently to question the results for deguelin obtained by those methods.

### Experimental Method

In a recent paper Goodhue and Haller (4) have shown that inactive deguelin forms stable solvates in the same manner as does rotenone, and the procedure described here is based on a method of separation of the desired substance in the form of the carbon tetrachloride solvate which can be conveniently weighed. An extract of the ground material is freed of aqueous alkali-soluble substances and rotenone, leaving the resin containing the deguelin. The resin is then treated with dilute alcoholic alkali to change the deguelin into the crystalline racemic form, which is purified by crystallization from carbon tetrachloride and weighed as the 1 to 1 solvate. The purity is determined by the red-color test.

**MATERIALS.** The analyses were made on seven samples of derris, five of cube, and one of timbo. The derris was for the most part taken from finely ground commercial samples. The variation from sample to sample was expected to be great, since commercial derris is obtained from a number of species and varieties. Two authentic samples of *Derris elliptica*, 4175 and 4176, and one sample of *Derris malaccensis*, 4177, were obtained from the Department of Agriculture of the Federated Malay States and Straits Settlements. The samples of cube and timbo (*Lonchocarpus*) were obtained from commercial sources.

**PROCEDURE.** Fifty grams of finely ground material that contains deguelin are extracted with chloroform in a Soxhlet for 7 hours. Nearly all the chloroform is evaporated on the steam bath, and the extract is taken up in about 75 cc. of ether. The ether solution is extracted with two 15-cc. portions of 5 per cent potassium hydroxide saturated with sodium chloride. The two portions of alkali are extracted with ether, and this ether, combined with the first portion, is washed once with 1 to 10 hydrochloric acid and once with a saturated sodium chloride solution. The alkali-soluble extract is discarded.

The ether is removed on the steam bath, and the resin is taken up in 40 cc. of carbon tetrachloride. This solution is seeded with

the rotenone-carbon tetrachloride solvate and allowed to crystallize overnight at 0° C. The solvate is then filtered and washed twice with 10-cc. portions of ice-cold carbon tetrachloride. This solvate may be used for the determination of rotenone if desired. The filtrate is evaporated on the steam bath to remove the carbon tetrachloride and taken up in 10 to 15 cc. of methanol. This solution is put while warm in a 25-cc. Erlenmeyer flask, and 10 drops of 40 per cent potassium hydroxide are added. The contents are swirled to mix, and the flask is carefully filled with warm methanol. A one-hole stopper carrying a funnel made from a drawn-out test tube is immediately inserted.

If the stopper is inserted properly, no air bubbles remain in the flask and some of the colorless liquid is forced up into the funnel. More methanol is poured in the funnel to take care of the contraction of the liquid on cooling and as a reserve for evaporation. The methanol solution should be kept at about 45° C. for an hour to prevent separation of resin before it is racemized. If deguelin is present, crystals soon separate, but racemization is usually not complete until the material has stood overnight.

The flask of racemized deguelin is cooled at 0° C. for 1 hour. The methanol is then decanted through a small filter and allowed to drain as completely as possible without being washed. For purification the deguelin crystals are dissolved in a little chloroform, and the chloroform is replaced by evaporating to a thick solution twice with carbon tetrachloride. Finally the deguelin is crystallized from either 5 or 10 cc. of carbon tetrachloride, depending on the amount present. It is usually necessary to seed the solution with the carbon tetrachloride solvate of deguelin at 0° C. and let it stand overnight for complete crystallization. The crystals are then filtered on a tared Gooch crucible, washed with cold carbon tetrachloride saturated with deguelin, air-dried at room temperature for 4 hours, and weighed as the 1 to 1 deguelin-carbon tetrachloride solvate.

The amount of deguelin in the impure solvate is determined by the red-color test (3). It is assumed that deguelin alone is responsible for the color, and the fact that racemic deguelin gives only 80 per cent of the color of rotenone is taken into consideration when rotenone is used as the standard of comparison.

The solubility of racemic deguelin in methanol and carbon tetrachloride was determined at 0° C. Saturated solutions were prepared at 40° C., cooled to 0°, and seeded. After standing overnight, they were filtered by gravity in the cold room, and the amount of deguelin was determined by the Goodhue red-color test. The carbon tetrachloride solution contained 0.25 gram and the methanol solution 0.11 gram of deguelin per 100 cc.

In calculating the results, the effect of these solubilities is compensated for by adding 0.08 per cent when only 5 cc. of carbon tetrachloride are used and 0.11 per cent when 10 cc. are used.

**A method for isolating and determining deguelin in derris and cube is proposed. After the rotenone and the aqueous alkali-soluble materials have been removed, the remaining resin is treated with dilute methanolic alkali. The resulting racemic deguelin is crystallized from carbon tetrachloride and weighed as a 1 to 1 solvate. The purity of the solvate is determined by the Goodhue red-color test.**

The amount of deguelin in different samples of derris and cube varies greatly. Eight out of the thirteen samples that were analyzed contained less than 1 per cent. One sample of derris contained 3.9 per cent, and one gave the low value of 0.24 per cent. The samples of cube examined varied in deguelin content from a high of 2.3 to a low of 0.25 per cent. The high toxicity to insects of the noncrystalline portion of derris and cube extracts, coupled with a generally low deguelin content, suggests the presence of other unidentified compounds that contribute to the toxicity.

### Results

The results of duplicate analyses by the racemization method are given in Table I. The deguelin content ranged from 0.25 to 3.29 per cent. A derris of very high rotenone content, sample 4176, contained the most deguelin. Very low results occur among both derris and cube samples.

For comparative purposes the amount of deguelin by the red-color test is given for all the samples and the amount by the dehydro method for five samples. In general the deguelin content is highest by the red-color method; the amount based on the weight of the dehydro compounds is slightly lower, while the results by the new racemization method are the lowest. The amount of deguelin found by this method is extremely variable, even when compared on the basis of the total extractives.

The small amount of deguelin obtained by racemization as compared with the amount indicated by the Goodhue red-color test suggests the presence of other unidentified compounds. Derride (11), called "elliptone" by Harper (6), is probably responsible for some of the additional red color, but not all, since little or no crystalline material was obtained by racemization. Some of these resins are being fractionated by molecular distillation, and the results of this investigation will be reported later.

### Discussion of Accuracy

While it is difficult to determine the absolute accuracy of a method of this type, an effort has been made to check each step and to show that no great error has been introduced.



TABLE I. DEGUELIN CONTENT OF DERRIS AND CUBE BY VARIOUS METHODS

Sample	Carbon Tetrachloride Solvate Grams	Deguelin in Carbon Tetrachloride Solvate %	Deguelin <sup>a</sup> by Racemization Method %	Deguelin by Red Color <sup>b</sup> %	Deguelin from Dehydro Compounds <sup>b</sup> %	Rotenone <sup>b</sup> %	Total Chloroform Extract <sup>b</sup> %
Derris 3002	0.6925	61	0.95	4.2	3.1	2.0	12.6
	0.6430	59	0.87				
3006	0.9463	59	1.23	6.0	4.2	3.6	16.5
	1.2025	58	1.51				
3833	0.3505	51	0.44	4.7	...	4.6	14.0
	0.3646	52	0.46				
4174	0.2529	45	0.31	2.6	...	3.3	12.8
	0.3364	45	0.38				
<i>Derris elliptica</i> 4175	1.9420	67	2.71	12.7	...	6.8	23.4
	1.8540	67	2.56				
4176	3.0630	62	3.91	10.3	...	11.7	27.0
	2.7640	69	3.92				
<i>Derris malaccensis</i> 4177	1.2180	64	1.67	4.8	...	5.6	26.3
	1.3649	57	1.67				
Cube 940A	1.6740	56	1.98	9.0	...	8.6	20.0
	1.5795	52	1.75				
3004	0.3913	40	0.38	3.0	3.1	2.6	16.4
	0.5538	40	0.52				
3005	2.3473	47	2.32	5.8	5.1	5.6	18.4
	1.8984	54	2.16				
M 1	0.1780	49	0.25	4.0	...	2.2	13.1
	0.1977	50	0.27				
M 2	0.2730	54	0.38	6.5	...	3.9	22.6
	0.5428	45	0.57				
Timbo 3230	0.5800	44	0.59	4.1	3.4	3.9	19.2
	0.5316	48	0.59				

<sup>a</sup> A correction of 0.11 per cent was added for the solubility where 10 cc. of carbon tetrachloride were used for crystallization. Samples obviously containing small amounts, less than 0.6 per cent, require only 5 cc. and thus a correction of 0.08 per cent.

<sup>b</sup> Some of these values were taken from published (8) and unpublished data by H. A. Jones, of this bureau.

First, the possibility that residual rotenone might be carried over was checked by determining the rotation of several of the deguelin-carbon tetrachloride solvates. Only a slight levorotation was observed, which indicated the presence in the solvate of only about 1 to 3 per cent of its weight, calculated as rotenone. This is considered negligible and might even help to correct for some small negative errors.

The possibility that much of the deguelin might be destroyed during racemization with dilute alkali was investigated. By high-vacuum distillation a concentrated sample of active deguelin was prepared from cube sample 3005. This gave a red-color value indicating the presence of 79 per cent of deguelin, and 50 per cent of the material was separated as the crystalline *l*-dihydrodeguelin after hydrogenation. Upon racemization, 83 per cent of inactive deguelin was obtained. The deguelin so obtained melted at 167° C. (corrected), and its crystallographic properties checked those of an authentic sample. Thus it appears that not more than 17 per cent can be destroyed by racemization, and such loss is probably much less, since the active deguelin sample used was not pure.

To show the contrast with a low-deguelin sample, derris 3833 was used to prepare a concentrate in the same way. The red-color test indicated that this sample apparently contained 60 per cent of deguelin, but no crystalline material could be obtained by racemization.

As in the rotenone analysis (7), an excess of resin might retard or prevent complete crystallization. To show the effect of time, one sample of derris 4176 was allowed to racemize for 3 days and to crystallize from carbon tetrachloride for the same time. No difference was noted. This also shows that long contact with dilute methanolic alkali in the absence of oxygen does not destroy the deguelin.

In many instances some resinous material adheres to the racemized deguelin, and in order to avoid loss the crude crystalline product is not washed. If the resinous material clinging to the crystals contains deguelin, it is recovered dur-

ing the carbon tetrachloride crystallization. The amount of resinous substances in the final crystallization is not very great and is not expected to have much influence on the solubility of the solvate.

An attempt was made to separate the active deguelin from the other resins in derris 4176. A sample was prepared as outlined above up to the point of racemization and then distilled in the high-vacuum still at 0.0005-mm. pressure. The distillate, amounting to 4.1 grams, was dissolved in ether to remove any dehydro compounds, but none separated. The ether was removed, and the resin was racemized in methanol as usual. A bulky mass of deguelin crystals separated within 10 minutes after the addition of alkali, but they were not filtered until the following day. Crystallization from carbon tetrachloride gave 1.834 grams of the deguelin solvate, which if pure indicates a deguelin content of only 2.64 per cent. About 32 per cent of the deguelin was lost in the distillation process.

In the final step, the use of the red-color test eliminates the error due to dehydro compounds and to tephrosin which probably appear in the final precipitate. Some degradation products of deguelin or rotenone may also give the red color, but since by this test the deguelin present in the solvate has never been more than 69 per cent as compared with the theoretical 71.9, it appears that little or no material that might add to the color is present.

The compound derride (11) should not interfere, since it does not form a solvate with carbon tetrachloride. After racemization it may cause some discrepancy, but insufficient information about this compound is available to justify any assumption at this time.

Finally, in the calculation of the results the solubility of deguelin in both methanol and carbon tetrachloride has been determined and the appropriate corrections have been made. These amount, at the most, to only 0.11 per cent.

### Precision

The precision is about equal to that in the rotenone analysis (10). The agreement is not quite so good, owing to the large number of transfers and operations that are necessary. Duplicate analyses should check to about 0.2 per cent. Many of the check determinations were made as much as one month apart, and the results were always in good agreement.

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# Quantitative Absorption Spectrophotometry

## An Internal Control Method

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IN ORDER to take advantage of the successful applications of emission spectrochemical analysis of metallurgical and chemical materials, many industrial and university laboratories are now equipped with apparatus suitable for this work. In a number of these laboratories absorption spectroscopy would also be useful, but, unless the number of applications available is considerable, few laboratories will incur the expense of an accurate spectrophotometer. Moreover, the critical adjustment of this instrument renders practically inefficient the frequent alternations required in a control laboratory where the same spectrograph is used both for emission work and as an adjunct to an absorption spectrophotometer.

An internal control method of photographic spectrophotometry was developed which permits the quantitative determination of extinction coefficients, or of percentage absorption, to be made rapidly with the same apparatus and general technique used for quantitative emission spectrochemical analysis. While this method may be used to determine the complete absorption curve of a material, it is most suitable for quantitative analysis in which the extinction coefficients need be determined at only one or a few wave lengths.

Representative chemical applications include determination of the amount of polymerization of resins, analysis of industrial organic chemicals for constituents or impurities, analysis of blood serum for the different hemoglobin compounds, and following the course of chemical reactions.

### Conventional Methods

The absorption of radiation by a material is given by the combined expression for Lambert and Beer's law

$$I = I_0 \times 10^{-kcl}$$

where  $I_0$  = intensity of radiation incident upon the material

$I$  = intensity transmitted by thickness,  $l$ , of the material

$c$  = concentration of the absorbing substance in the material

$k$  = specific extinction coefficient (extinction coefficient for unit concentration and unit thickness)

Since the value of  $k$  is ordinarily independent of  $c$  and  $l$ ,  $k$  is the most suitable quantity for the measurement of the quantitative absorption of radiation by a material.  $k$  may be obtained by photographic or photoelectric methods in the ultraviolet region, and also by visual methods in the visible region of the spectrum.

In the usual photographic method of spectrophotometry two light beams from the same source simultaneously reach the spectrograph slit. One beam, which traverses the absorbing material, is maintained at constant intensity; the other, which traverses the comparison material, may be arbitrarily varied in intensity. A series of photographs is taken on the same plate with the intensity of the latter beam varied over the desired range. Each of these photographs consists of a pair of adjacent spectra, one of normal intensity, the other of varied intensity. The percentage absorption, or the extinction coefficient, produced at any wave length by the absorbing material is determined by visually, or microphotometrically, finding which pair of spectra shows equal density at that wave length. Since the extinction coefficients are

obtained by density matches made upon only adjacent spectra, high accuracy is obtained only by simultaneous photography of the two spectra. A large number of pairs of spectra are ordinarily required to determine the extinction coefficient, at a selected wave length, of a sample of known qualitative, but unknown quantitative, composition.

In visual spectrophotometry, two beams from the same light source pass simultaneously through the absorbing and comparison materials, and adjacent spectra of the two beams are formed by means of a suitable optical system and a spectrometer. The amount by which the intensity of the comparison beam must be reduced by suitable means, in order to equalize the intensities of the two beams, in the small wave-length region selected, gives the measure of the absorption.

In the photoelectric technique only one light beam is used. The intensities at a selected wave length, of the spectra, produced by a monochromator, of the absorbing and comparison materials are measured in succession with a photo-cell-electrometer arrangement. High accuracy requires a light source of very constant intensity and great intrinsic brightness.

### Internal Control Method

**BASIS OF METHOD.** Unless a critically adjusted, dual optical path is used so that the spectra of the absorbing and comparison substances can be simultaneously photographed or visually examined, or a two-photocell, "null" arrangement can be employed, the situation present in the three conventional methods described is analogous to that found in quantitative emission spectrochemical analysis before the use of internal control elements. The success of spectrochemical analysis, since the introduction of the use of radiation intensities and of internal controls, suggested similar use of these two quantities in quantitative photographic spectrophotometry.

The comparison of the radiation intensities, at any wave length, transmitted by the absorbing and comparison materials, is made by a method of internal control. The basis of the method is the determination of the relative intensity of selected wave lengths, one within an absorption band of the material, and the other in a region, in which there is no absorption, of the spectrum of the material. The true absorption is obtained by equalizing the effective exposures of the absorbing and comparison materials by subtracting from the log intensity ratio of the selected, unabsorbed internal control wave length to the absorbed wave length in the absorption spectrum the ratio for the corresponding wave lengths in the comparison spectrum.

If the intensity of the light source and the exposure conditions can be maintained sufficiently constant, the absorption may be obtained by a direct intensity comparison, at the same wave length, of the absorption and comparison spectra ( $I$ ). By this means, however, all of the advantages of the internal control technique are lost.

In the internal control method, spectra of the comparison material and of the different absorbing materials under test are photographed on the same plate. Identical intensities and exposure times are not required. A sixfold inequality in the exposure times for the absorbing and comparison materials was found, in a representative example, to produce no

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error in the value of the extinction coefficient. An intensity calibration of each plate is made by means of a step-slit, a rotating step-sector, or a number of selected lines in a spectrum for which intensities have been measured by one of these methods. The blackenings of the selected wave lengths and of the steps of the calibration pattern are measured microphotometrically. From the blackenings of this pattern the characteristic curve of the plate is drawn. The logarithms of the relative intensities of the pairs of selected wave lengths are obtained by applying their measured blackenings to this curve. From these log intensity ratios the extinction coefficient of the absorbing material is readily determined.

**EXPERIMENTAL CONDITIONS.** *Sample.* If the material under test is a liquid, powder, or irregular solid, it may be dissolved in a suitable solvent. The solution and solvent are placed, in succession, in a cell containing plane quartz windows and the absorption spectrum of each is photographed. If the material is a film, plate, or block of uniform thickness, its absorption spectrum may be photographed directly. In this case the comparison substance may be the nonabsorbing support, a quartz plate, or air.

*Light Source.* Light sources which emit either continuous or line spectra may be used. The former is useful for the detection and identification of absorption bands, but the latter is preferred for quantitative analysis because of (1) ease of selection of the same wave length in each spectrum, (2) ease of selection of an internal control wave length of suitable density, and (3) simplicity and durability of line spectrum sources.

Several types of line spectrum sources may be used. These include condensed sparks between suitable metallic electrodes, and metallic vapor or gas discharges. For the determination of the absorption of materials which possess absorption bands at suitable wave lengths a low-voltage mercury arc and, particularly, a helium lamp (2) powered by a neon sign transformer should be, because of their very constant intensities, especially favorable sources.

*Selection of Wave Lengths.* The absorbed wave length selected for use in quantitative analysis should be at, or near, the peak of a band. The internal control wave length should be chosen as in emission spectrochemical analysis, but, since all wave lengths used are radiated by the same element, fewer conditions need be fulfilled than in emission analysis.

**EXTINCTION COEFFICIENTS.** With the present technique, three different extinction coefficients may be considered.

1. Specific extinction coefficient,  $k$

$$k = \frac{\log_{10} \frac{I_0}{I}}{c l}$$

where  $I$  = intensity of radiation transmitted by  $l$  cm. of the material at an absorbed wave length,  $\lambda_a$

$I_0$  = corresponding intensity transmitted by the comparison substance

$c$  = concentration of the absorbing substance in the material

$k$  gives the true value of the absorption and is obtained by an intensity comparison, at the same wave length, of the absorption and comparison spectra. For high accuracy these two spectra must be produced simultaneously by the same source and photographed under absolutely identical conditions.

2. Reference specific extinction coefficient,  $k_1$

$$k_1 = \frac{\log_{10} \frac{I_2}{I}}{c l}$$

where  $I_2$  = intensity transmitted by  $l$  cm. of the material at an unabsorbed internal control wave length,  $\lambda_c$

$k_1$  is thus obtained by an intensity comparison of the absorption band and internal control wave lengths in the spectrum of the material.  $k_1$  gives an empirical measure of the absorption which

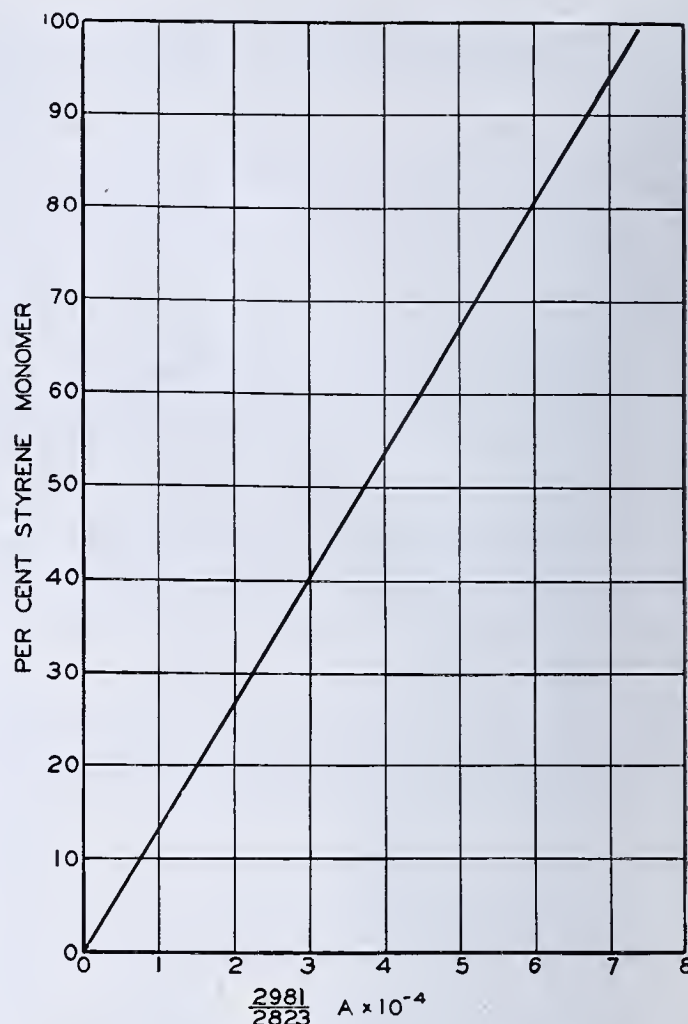


FIGURE 1. ANALYTICAL CURVE FOR DETERMINING MONOMER CONTENT OF PARTIALLY POLYMERIZED STYRENE

Internal control wave length,  $\lambda_c$ , 2980.53 Å. Absorbed wave length,  $\lambda_a$ , 2823.28 Å.

will be of value, provided  $l$  and  $c$  remain constant for all determinations.

3. Compensated specific extinction coefficient,  $k_2$

$$k_2 = \frac{\log_{10} \frac{I_2}{I} - \log_{10} \frac{I_1}{I_0}}{c l}$$

where  $I_1$  = intensity transmitted by the comparison substance at the internal control wave length,  $\lambda_c$

$k_2$  is thus obtained by a method of internal control which, by eliminating the effects of any variations between the comparison and absorption exposures and of changes in the light source intensity, permits an accurate intensity comparison, at the same wave length, to be made between the comparison and absorption spectra without the necessity for simultaneous exposure. Since the above expression for the evaluation of  $k_2$  equalizes the effective exposures of the absorbing and comparison materials, neither of which absorbs at the internal control wave length,  $k_2$  is identical in value with  $k$  and gives the true value of the absorption.

The absorption of a material expressed in terms of  $k_2$  or  $k$  obeys Beer's law, but that expressed in terms of  $k_1$  does not.

**QUANTITATIVE ANALYSIS.** The analysis of a sample for a constituent which possesses an absorption band in the photographic region is made directly by means of the analytical extinction coefficient,  $A$

$$A = \frac{\log \frac{I_2}{I} - \log \frac{I_1}{I_0}}{s l}$$

where  $s$  equals the concentration of the total sample in the material, of thickness,  $l$ , of which the absorption spectrum is obtained.



If the sample, which contains an absorbing constituent, must be dissolved in a suitable solvent to obtain its absorption spectrum,  $s$  is the concentration of the solute in the solvent.  $c$  is the concentration of the absorbing constituent, only, in the solvent. If the spectrum of the sample may be obtained directly,  $s$  is equal to unity. The analysis is standardized by establishing, by means of samples of known composition, the relationship between  $A$ , for a wave length in the absorption band, and the concentration of the absorbing constituent. The graph of this relationship provides an analytical curve, as shown in Figure 1. A sample of unknown concentration is analyzed by determining the appropriate  $A$  value from the measured relative intensities of the selected wave lengths, and reading the desired concentration from the analytical curve.

**PRECISION.** In the conventional photographic method of spectrophotometry, in which two adjacent spectra are compared visually, it is said to be possible to detect a difference in optical density of 0.06 (4). Thus by the use of an Eastman Polychrome plate (as processed in the present work) of  $\gamma = 0.45$ , a difference of 0.13 in the density of the absorbing substance should be detected. The precision of density determination, which is limited by only the photometric error, with the present technique permits the detection of a density difference of 0.009 in the absorbing substance.

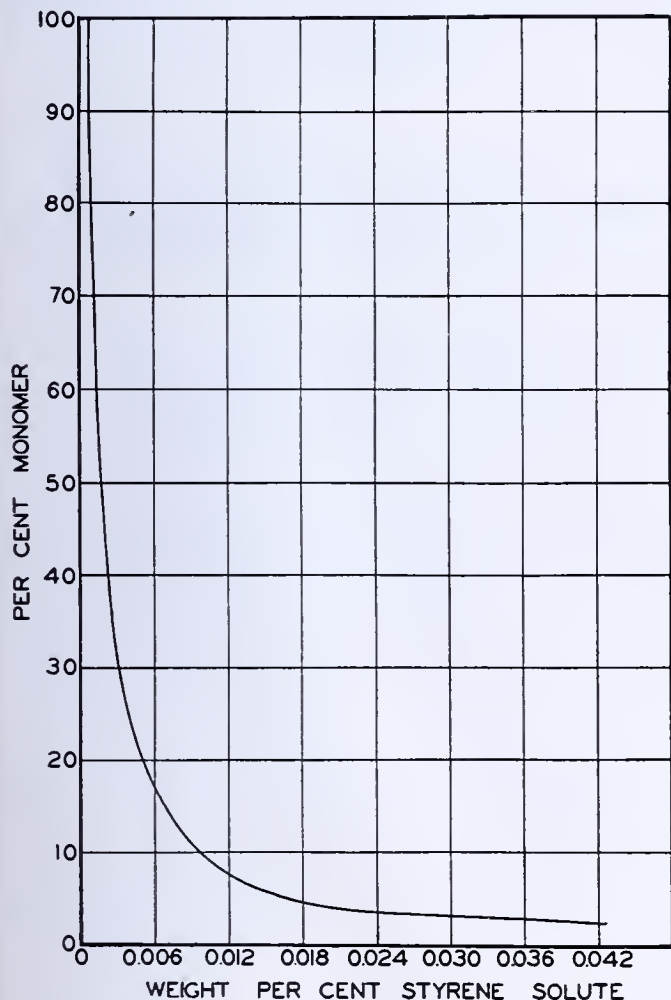


FIGURE 2. OPTIMUM SOLUTION CONCENTRATION FOR ANALYSIS FOR MONOSTYRENE

Data obtained from routine analyses for monostyrene showed that the average error in the determination, from one spectrum, of the extinction coefficient

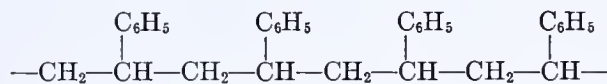
$$K = \frac{\log_{10} \frac{I_0}{I}}{l}$$

was approximately  $K = 0.006$  over the range of  $K$  values from 0.08 to 0.12 ordinarily used in this analysis. The average of three spectra will reduce the error by half. Approximately one half of the error lies in the photometry and the nonuniformity of the photographic plate. Most of the remainder of the error is accounted for by the small random variations in the relative intensities of the spectral lines emitted by the iron condensed spark light source used.

### Representative Applications

**ANALYSIS OF PARTIALLY POLYMERIZED STYRENE FOR MONOMER CONTENT.** The determination of the amount of polymerization of synthetic resins, and other polymerizable compounds, is of considerable importance for the control of the polymerization process.

Styrene,  $C_6H_5-CH=CH_2$ , is a typical polymerizable material. Its polymer has the probable structure (3)



Absorption spectra revealed that monomeric styrene possessed absorption bands at 2910 Å. and at 2830 Å., and complete absorption at wave lengths shorter than 2690 Å. Polystyrene was found to have a band at 2695 Å., and complete absorption below 2400 Å.

Since the intensities of the absorption bands of the monomer were found to increase regularly with increasing monomer percentage, the absorption technique described was applied to the quantitative analysis of partially polymerized styrene for the monomer content.

The partially polymerized styrene samples, in either liquid, as polymerized, or alcohol-precipitated form, are dissolved in chloroform to definite concentrations. With the experimental conditions used, approximately 0.013 mg. of monomer per cc. of chloroform gives absorption band intensities most suitable for accurate photometry. Figure 2 shows graphically the relationship between the monomer percentage and the weight per cent of solute (partially polymerized styrene sample) for this optimum monomer concentration. It is, however, not necessary to employ only the optimum concentration, since it has been found possible in practice to cover the entire monomer concentration range satisfactorily from 0 to 100 per cent by the use of only four solution concentrations, 0.0015, 0.005, 0.02, and 0.05 weight per cent of solute.

The solution contained in a quartz cell of 2-cm. length, fitted with plane quartz windows, is placed between an iron condensed spark discharge and the slit of a medium quartz spectrograph. The absorption spectra of the test solutions and of the solvent are photographed and the intensities of the absorption bands of monostyrene, as recorded on an Eastman Polychrome plate, are measured. These absorption band intensities are obtained by intensity comparisons, by the technique described, of the iron lines 2912.16 Å. and 2823.28 Å., which lie near the peaks of the two bands, with the internal control iron line 2980.53 Å. The analysis is standardized by an experimental correlation of the analytical extinction coefficient,  $A$ , for 2823 Å. with the monomer percentage, as shown in Figure 1. The value of  $A$  for 2912 Å. may also be used as a check, if desired.

Partially polymerized styrene may be analyzed for a monomer content of from 0 to 100 per cent. The representative precision and accuracy given by a single spectrum are shown in Table I. By precision is meant the average deviation of the monomer percentage given by a single spectrum from the mean result given by all the spectra of that sample. By accuracy is meant the average deviation of the monomer percentage given by a single spectrum from the true amount



TABLE I. PRECISION AND ACCURACY OF ANALYSIS FOR MONOMERIC STYRENE

Actual Monomer Percentage	Precision		Accuracy	
	Average error, % monomer	Average % error	Average error, % monomer	Average % error
0.58	0.05	8.6	0.085	14.7
1.09	0.07	5.9	0.11	9.7
5.07	0.13	2.6	0.13	2.6
10.08	0.34	3.4	0.35	3.5
30.0	1.0	3.3	1.45	4.8
70.0	1.7	2.4	2.0	2.9
100.0	5.3	5.3	7.5	7.5

present. These data were obtained from a total of nine spectra for each sample photographed on four plates.

The average error, expressed as per cent monomer, increases with increasing monomer concentration on account of the constancy of the photometric error, the linearity of the analytical curve, and the decreasing percentage of solute used. The magnitude of the error lies within that which might be caused by photometric errors and the nonuniformity of the photographic plate.

The accuracy obtained, particularly in the commercially important range from 0 to 10 per cent monomer, is sufficient for routine practical analysis.

One sample may be analyzed in a total elapsed time of 2 hours, while ten samples may be analyzed in 6.5 hours. The number of man-hours of work required is approximately 60 per cent of the total elapsed time. The time taken for

the preparation of the solutions accounts for one half of the total time required.

**OTHER APPLICATIONS.** Other applications for which this method should be particularly suitable include:

1. The important problem in the petroleum industry of the determination of the amount of aromatic impurities in aliphatic and alicyclic compounds.
2. The determination of the amounts of the different hemoglobin compounds in blood serum.
3. The following of the course of polymerization, and of other chemical reactions, in which the reactions involved produce changes in the intensities of characteristic absorption bands of the reactants or produce products which possess new absorption bands.

### Acknowledgment

The writer wishes to express his thanks to Jacob Heerema for assistance in obtaining the experimental results of this paper.

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# Analysis of Organic Materials for Traces of Metallic Impurities

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**R**APID, accurate analysis for small traces of metallic impurities is an important factor in the manufacture of modern organic chemicals. For this reason the spectrochemical analysis of such materials, including cellulose derivatives, synthetic resins, pharmaceuticals, dyes, and biological tissues and fluids, has been developed for traces of aluminum, calcium, copper, iron, lead, magnesium, manganese, nickel, strontium, tin, and zinc. The determination of some of these elements in the presence of others, in their natural ranges of abundance, is very difficult, if not impossible, by chemical methods. The spectrochemical method is not thus limited and gives good precision in the low concentration range of interest. Moreover, the spectrochemical analysis effects an important saving of time, since the analyses for all the test elements may be carried out by measurements made upon one spectrum.

This technique is not limited to the eleven test elements mentioned, but may be used to determine practically all of the metallic and metalloid elements. While the application of the method to organic materials is specifically described, it is readily evident that, since the actual sample analyzed is a solution of inorganic salts, the same method and in some instances even the same analytical curves, may be used for the analysis of many inorganic materials.

### Analytical Technique

**GENERAL METHOD.** The analytical technique used is the well-known internal control method (5) in which the analysis is made from photometric measurements of the relative in-

tensities of the spectral lines of the test elements and of the internal control elements introduced into each sample in constant amount. This relative intensity is a measure of the concentration of the test element. The actual relationship is determined for each element by measurements made upon the spectra of a series of specimens of known composition in which the test elements vary over the desired ranges of abundance. The graph of this relationship, illustrated in Figure 1, provides an analytical curve for the determination of that element.

**PREPARATION OF SAMPLES.** In order to obtain maximum analytical sensitivity and accuracy it has been found necessary to remove the organic matter by wet-ashing in spectroscopically pure nitric, sulfuric, and perchloric acids. The resulting solution is evaporated nearly to dryness, and the residue is taken up in a definite volume of a solution containing the spectroscopic buffer and the internal control elements. The spectroscopic buffer is an added amount of a suitable salt which eliminates the effects upon the analysis of the extraneous composition of the samples and permits the use of the same analytical curves for the analysis of samples which vary considerably in composition (7).

The following standard procedure has been adopted:

A 0.4-gram sample of the test material is weighed out on a watch glass and transferred to a 150 × 20 mm., Pyrex test tube or a 30-ml. Kjeldahl flask. After the addition of 1 ml. of concentrated sulfuric acid the test tube or flask is placed on a sand bath heated by gas burners. The sample is heated until charring is complete, after which concentrated nitric acid is added to aid in completing the oxidation. The nitric acid is added to the hot

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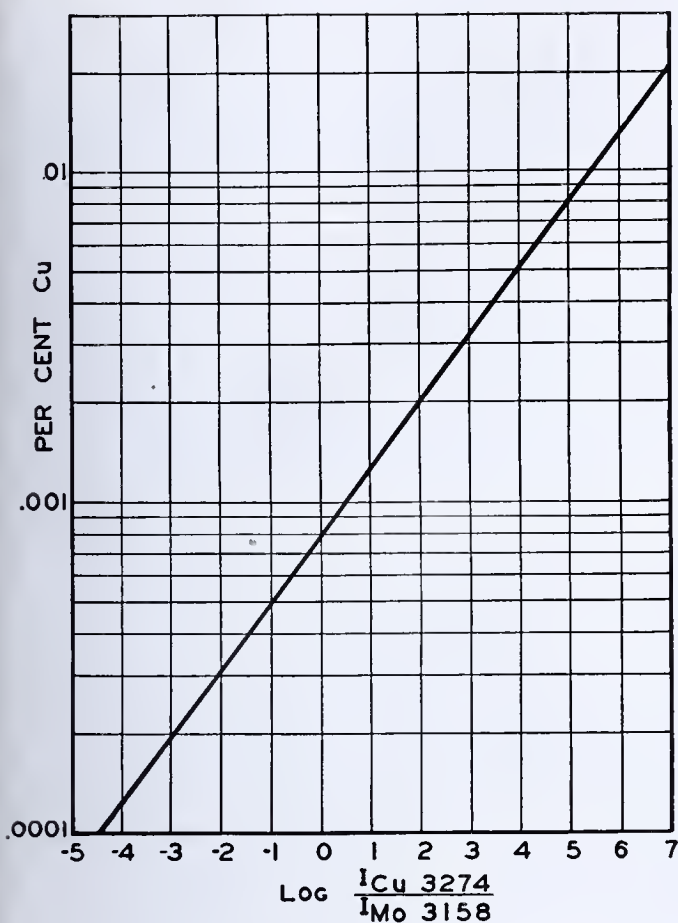


FIGURE 1. REPRESENTATIVE ANALYTICAL CURVE

mixture a few tenths milliliter at a time until the solution becomes water-clear, denoting complete oxidation. In case the sample is particularly difficult to oxidize, shown by the persistence of a dark brown coloration in the concentrated solution, a few tenths milliliter of concentrated perchloric acid is added to the sulfuric-nitric acid mixture after most of the free carbon has been destroyed. The perchloric acid produces more rapid completion of the oxidation. The average sample may be ashed by this procedure in 10 minutes, while a similar technique applied to a larger sample (5 to 10 grams) will require from 30 to 45 minutes. The use of the smaller sample and of the correspondingly smaller equipment and amounts of acid also reduces the chance of contamination during the ashing process.

When the solution becomes water-clear, it is evaporated to dryness to remove all sulfuric acid. The tube is cooled and 1 ml. of concentrated nitric acid is added. This solution is evaporated almost to dryness. Overheating is avoided at this point, since some of the nitrates decompose rather readily, forming salts of low solubility. Excess heat may also change the form of some salts in such a manner as to affect the relative intensities of the spectral lines used in the analysis.

The residue is taken up in 0.4 ml. of a 2 N nitric acid solution containing the spectroscopic buffer and the internal control elements, bismuth and molybdenum.

The arc electrodes are prepared as follows: Pure graphite rods 0.635 cm. (0.25 inch) in diameter are cut into 1.25-cm. (0.5-inch) lengths. The edges of one end of each section are slightly beveled and the end is polished on a clean paper towel. One drop of redistilled kerosene is added to the polished end of each section and allowed to evaporate. Each of a pair of the sections is then loaded with 0.03 ml. of the test solution. The electrodes so prepared are placed in a sheet-metal rack and dried for 1 to 2 minutes directly over a small gas flame. Dried properly in this manner the salt will form a smooth tenacious mass which uniformly covers the entire end of the rod. The electrodes may also be dried by placing them in an indirectly heated oven at a temperature of approximately 70° C. and gradually raising the temperature to 110° C. They will dry satisfactorily in this manner in about 15 to 20 minutes.

**LIGHT SOURCE.** The successful applications of the high-voltage, alternating current arc (1) in the authors' laboratory suggested its use for this analysis. Tests showed that this source was superior in sensitivity and precision to the direct current arc, and that it was entirely suitable for this work.

The circuit used has been previously described (9, 10), and is identical with that used by Duffendack and his co-workers (2, 4), except for the introduction of a primary inductance of 0.006 henry. The screw-controlled arc stand, which permits accurate spacing of the electrodes, has been described (4). The sensitivities given by arc currents of 2.5, 4.0, and 6.0 amperes were found to be approximately equal. Since the 4.0-ampere current gave a suitable exposure, with the medium quartz spectrograph employed, in a convenient time without too rapid volatilization of the sample, this current was chosen for use. After 30 seconds of arc operation the electrode spacing is set accurately at 0.75 mm. and exposures of 10 and 45 seconds are taken on Eastman Polychrome plates.

Determination of Analytical Curves

Biological materials have been analyzed for sodium, potassium, calcium, magnesium, and lead by means of essentially the same light source and a technique similar to that used here (2). The procedure used for the lead determination was, however, different from that used in the analysis for the other elements. The present analysis, which involves the determination by exactly the same procedure, of numerous impurity elements in a variety of industrial and biological organic materials, posed a somewhat different and more difficult problem. The major portion of this investigation has been devoted to the problem of setting up analytical curves which will yield accurate analyses regardless of great changes in the extraneous composition of the sample.

**CHOICE OF INTERNAL CONTROL ELEMENT.** The variety of the test elements and their small ranges of abundance prevented a successful choice of internal control element being made theoretically upon the basis of spectroscopic and physical data. The actual choice of the control element was made upon the basis of experimental tests of the constancy of the relative intensities of the lines of the test elements and of different control elements with duration of the arcing, of the densities and wave lengths of the spectral lines of these elements, and of the analytical precision obtained. The results of these experiments showed that no one control element would give satisfactory determinations of all the test elements, but that two control elements could be found which would suffice.

TABLE I. INTERNAL CONTROL ELEMENTS

Test Element	Control Element
Pb	Bi
Al, Zn	Mo or Bi
Ca, Cu, Fe, Mg,	Mo
Mn, Ni, Sr, Sn	

Previous experience with a number of internal control elements indicated that bismuth or molybdenum should be a suitable reference element for this analysis. Experiments made under the analytical conditions selected for use showed that, during an arcing period of 6 minutes, the lead intensity remained most constant with respect to bismuth, the aluminum and zinc intensities remained equally constant with respect to either bismuth or molybdenum, and the calcium, copper, iron, magnesium, manganese, nickel, strontium, and tin intensities remained most constant with respect to molybdenum. Accordingly, the control elements selected for use are given in Table I.

**EFFECT OF THE PRESENCE OF ONE ELEMENT ON THE ANALYSIS FOR OTHERS.** It has been previously found (3), that in dilute solutions of metallic salts, variations of the concentrations of certain elements affect the analyses for other elements and that the addition of an excess amount of an element of low excitation potential, such as an alkali metal, will sometimes decrease or eliminate this effect. A similar



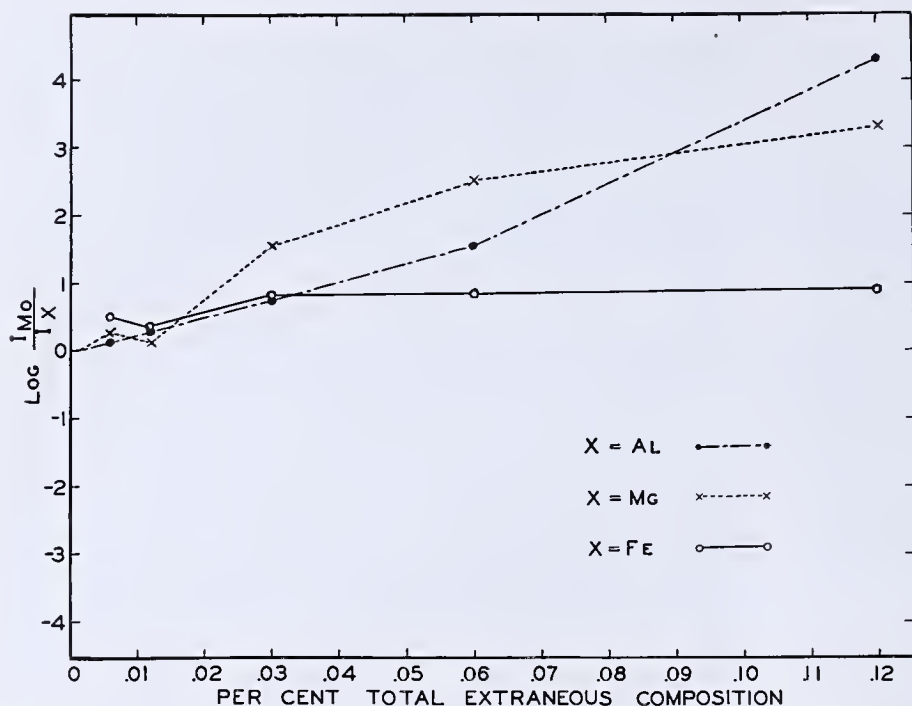


FIGURE 2. EFFECT OF EXTRANEEOUS COMPOSITION OF SAMPLE, SULFATE SOLUTIONS

interference, encountered in this investigation, indicated the necessity for the use of a suitable spectroscopic buffer, or excess element.

TABLE II. ANALYSIS OF ORGANIC MATERIALS

Impurity	Spectral Lines Impurity Å.	Control Å.	Range of Analysis %	Sensitivity (Impurity on Electrodes) Mg.
Al	3093	Mo 3158	0.0001-0.02	$6 \times 10^{-5}$
Al	3093	Bi 2898	0.0001-0.02	$6 \times 10^{-5}$
Ca	3934	Mo 3903	0.0001-0.0025	$6 \times 10^{-5}$
Ca	3179	Mo 2816	0.001-0.02	$6 \times 10^{-4}$
Cu	3274	Mo 3158	0.0001-0.02	$6 \times 10^{-5}$
Fe	3021	Mo 3158	0.0001-0.02	$6 \times 10^{-5}$
Pb	2833	Bi 2898	0.0001-0.02	$6 \times 10^{-5}$
Mg	2796	Mo 2816	0.0001-0.0025	$6 \times 10^{-5}$
Mg	2780	Mo 2816	0.001-0.02	$6 \times 10^{-4}$
Mn	2798	Mo 3158	0.0001-0.02	$6 \times 10^{-5}$
Mn <sup>a</sup>	2576	Mo 2816	0.0001-0.02	$6 \times 10^{-5}$
Ni	3415	Mo 3358	0.0001-0.02	$6 \times 10^{-5}$
Sr	4078	Mo 3903	0.0001-0.0025	$6 \times 10^{-5}$
Sr	3381	Mo 3358	0.001-0.02	$6 \times 10^{-4}$
Sn	3175	Mo 3158	0.0001-0.02	$6 \times 10^{-5}$
Zn	3345	Mo 3358	0.001-0.02	$6 \times 10^{-4}$
Zn	3345	Bi 3397	0.0005-0.02	$3 \times 10^{-4}$

<sup>a</sup> Used if Mg exceeds 0.005 per cent.

Since, at the beginning of the problem, the materials under analysis could be ashed in nitric acid, the final solutions of the ashed samples were left as nitrates. In order to be able to make, from the same spectrum, an occasionally required analysis for sodium, a suitable spectroscopic buffer, which did not contain this element, was first sought. The primary requirements for such a buffer are that it contain none of the test elements, either as a constituent or an impurity; that it contain a metal of sufficiently low excitation potential to maintain an arc of constant spectral character, regardless of the sample composition; and that it volatilize at a uniform rate during the entire arcing period. The buffers tried were selected upon the basis of previous work in this and other laboratories (6, 8, 11).

The concentrations of all the buffers added are expressed in percentages of the total solution weight. Ten per cent of lithium tartrate, which contains 0.77 per cent of lithium, was found to give no improvement in the constancy of the relative intensities. The next buffer tried, which consisted of a mixture of 8 per cent potassium

bromide and 2 per cent lithium tartrate, was no more effective than the previous one. A similar mixture of potassium bromide and tartaric acid gave no better results. Mixtures of potassium nitrate and ammonium nitrate in the following proportions were next employed: 2.75 per cent potassium as potassium nitrate and 27 per cent ammonium nitrate; 0.66 per cent potassium as potassium nitrate and 37 per cent ammonium nitrate. While either of these mixtures, during its persistence in the source, had considerably more effect than the previous two buffers in reducing the background density and improving the constancy of the relative intensities, its duration in the arc was too brief to improve the analyses materially. Five per cent sodium as sodium nitrate was found satisfactorily to eliminate the effect of sample composition and to permit sufficiently sensitive and accurate analyses to be made.

In order to enlarge the field of application to include nearly all organic materials, the addition of sulfuric acid to the ashing technique was made. This procedure left the solutions as sulfates. On account of the known difficulty of converting sulfates to nitrates and of the belief that the cation was the controlling constituent of the buffer, 5 per cent sodium as sodium sulfate was investigated. It was found that the effect of sample composition could not be eliminated nearly so completely in sulfate as in nitrate solutions, so that the use of the sulfate ion was unsuitable for the analyses of the test materials. The comparative effects of sample composition in sulfate and nitrate solutions are shown in Figures 2 and 3.

Since it was found that the effects of sample composition could be sufficiently eliminated to allow an accurate analysis by means of nitrate, but not by means of sulfate solutions, nitrate solutions and a sodium nitrate buffer were selected for practical use. It was found that the sulfate solutions present at the completion of any ashing involving sulfuric acid could be converted into nitrate solutions by first evaporating to dryness, dissolving the residue in concentrated nitric acid, and evaporating this solution almost to dryness. The residue, taken up in a 2 *N* nitric acid solution containing sodium nitrate and the internal control elements, comprises the analytical solution. The possible residual amount of sulfate ion is too small to affect the analyses.

RANGE OF ANALYSIS. The percentage ranges under analysis, the sensitivities, and the spectral lines of the impurity and control elements used are shown in Table II.

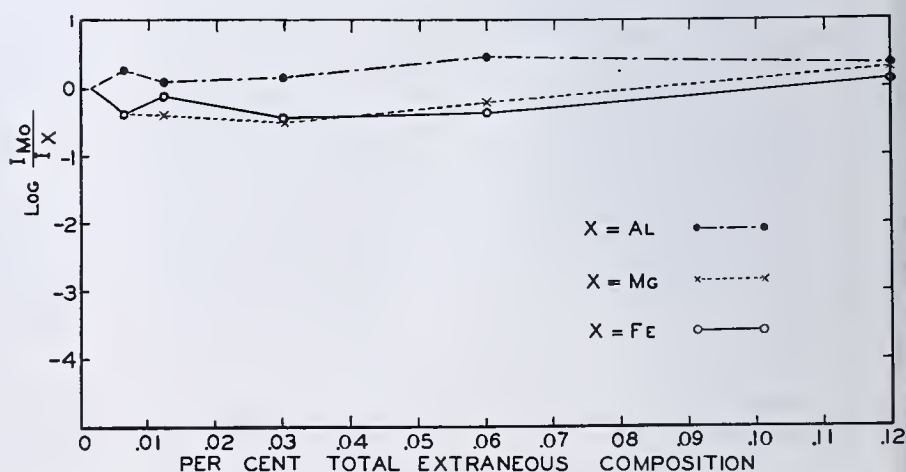


FIGURE 3. EFFECT OF EXTRANEEOUS COMPOSITION OF SAMPLE, NITRATE SOLUTIONS



TABLE III. REPRESENTATIVE PRECISION AND ACCURACY

Sample	Al %	Ca %	Cu %	Fe %	Mg %	Mn %	Ni %	Pb %	Sn %	Sr %	Zn %
A <sub>1</sub>	0.00046	0.00037	0.00050	0.00055	0.00048	0.00050	0.00055	0.00062	0.00058	0.00045	....
A <sub>2</sub>	0.00061	0.00052	0.00058	0.00062	0.00072	0.00054	0.00059	0.00044	0.00073	0.00059	....
A <sub>3</sub>	0.00048	0.00039	0.00055	0.00048	0.00048	0.00052	0.00050	0.00046	0.00048	0.00049	....
B <sub>1</sub>	0.0008	0.0010	0.0009	0.0008	0.0008	0.0008	0.0010	0.0009	0.0008	0.0010	0.0015
B <sub>2</sub>	0.0012	0.0011	0.0012	0.0012	0.0011	0.0010	0.0013	0.0010	0.0012	0.0010	0.0013
B <sub>3</sub>	0.0012	0.0011	0.0013	0.0011	0.0011	0.0011	0.0013	0.0009	0.0011	0.0011	0.0010
C <sub>1</sub>	0.0023	0.0020	0.0023	0.0022	0.0020	0.0022	0.0026	0.0020	0.0016	0.0024	0.0025
C <sub>2</sub>	0.0026	0.0023	0.0027	0.0026	0.0019	0.0025	0.0026	0.0024	0.0020	0.0025	0.0021
C <sub>3</sub>	0.0027	0.0023	0.0025	0.0025	0.0027	0.0025	0.0026	0.0020	0.0019	0.0027	0.0030
D <sub>1</sub>	0.0053	0.0057	0.0053	0.0056	0.0051	0.0048	0.0054	0.0049	0.0045	0.0050	0.0056
D <sub>2</sub>	0.0051	0.0054	0.0054	0.0051	0.0054	0.0047	0.0053	0.0045	0.0052	0.0048	0.0051
D <sub>3</sub>	0.0056	0.0046	0.0059	0.0061	0.0054	0.0050	0.0061	0.0044	0.0057	0.0052	0.0058
Known composition of samples: A <sub>1</sub> , A <sub>2</sub> , A <sub>3</sub> . 0.0005% of each element. C <sub>1</sub> , C <sub>2</sub> , C <sub>3</sub> . 0.0025% of each element.											
B <sub>1</sub> , B <sub>2</sub> , B <sub>3</sub> . 0.0010% of each element. D <sub>1</sub> , D <sub>2</sub> , D <sub>3</sub> . 0.0050% of each element.											

PRECISION AND ACCURACY. Representative precision and accuracy of the analysis are given in Table III. Each of the four samples, A, B, C, and D, was divided into three portions and each such portion was individually ashed and analyzed by means of duplicate spectra.

By means of the technique described, almost any organic material may be rapidly analyzed for the eleven test elements, in the range from 0.0001 to 0.02 per cent, with an average error of approximately 12 per cent of the amount present. If desired, the range of analysis may be extended to higher concentrations. Under the usual laboratory conditions, the time required for the determination of each test element is about 5 man-minutes.

Acknowledgment

The writers are indebted to the other members of the staff of the Spectroscopy Laboratory for experimental assistance in various phases of this work.

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Determination of Magnesium in Biological Materials

An Oxidation Method

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THE 8-hydroxyquinoline methods for the determination of magnesium have been used with a fair degree of success for a number of years (2, 3, 4). Probably the principal objection to these methods is in connection with the bromination of the 8-hydroxyquinoline. Greenberg, Anderson, and Tufts (3) have suggested a procedure involving special apparatus to prevent the loss of bromine.

Since the magnesium quinolate gives a precipitate of highly reproducible composition, any measurable reaction involving the organic part of the molecule might be used in the determination of the precipitated magnesium. The author has had considerable success in quantitatively oxidizing organic compounds with ammonium hexanitrate cerate. If the magnesium quinolate could be oxidized reproducibly, a method could then be devised, eliminating the troublesome bromination involved in previous methods and possibly attaining a lower equivalent weight for magnesium.

Experimental

A carbon tetrachloride solution of known 8-hydroxyquinoline content was prepared. Aliquots of this solution were placed in 50-ml. Erlenmeyer flasks and the carbon tetrachloride was evaporated by drawing air through the flask. When the solvent had disappeared, a known volume of standardized ammonium hexanitrate cerate in 2 M perchloric acid was added and the mixture was heated for varying lengths of time in a water bath held between 96° and 100° C. The solution was then cooled and the excess cerate titrated with standard ferrous ammonium sulfate, using o-phenanthroline ferrous sulfate as an indicator. Table I shows that the reaction goes to completion in 10 minutes.

A calculation based on these data showed that approximately 29 equivalents of cerate were used per mole of 8-hydroxyquinoline. Two molecules of quinoline are precipitated with each magnesium ion, thus making a factor of 58 as compared to a factor of 8 by the bromination procedure.



TABLE I. DETERMINATION OF MAGNESIUM

8-Hydroxyquinoline Mg.	Time Min.	Reagent Used per Mg. of 8-Hydroxyquinoline Ml.
0.50	10	3.76
0.75	10	3.84
1.00	5	2.60
1.00	10	3.70
1.00	15	3.75
1.00	30	3.80

TABLE II. DETERMINATION OF MAGNESIUM

MgO Added Mg.	0.0461 <i>N</i> Cerate per 0.10 Mg. of MgO Ml.
0.0870	3.21
0.0870	3.26
0.0870	3.28
0.0870	3.16
0.1220	3.28
0.0376	3.10
0.0752	3.22
Blank	0.15

TABLE III. AGREEMENT BETWEEN METHODS

Sample No.	MgO, 8-Hydroxy- quinoline Method P. p. m.	MgO, A. O. A. C. Method P. p. m.
1	149	146
2	168	168
3	116	117
4	152	154
5	173	173
6	184	181
7	157	148
8	164	168
9	183	177
10	182	183
11	143	148
12	193	192
13	224	218
14	159	160
15	174	170
16	179	178
17	146	142
18	195	194
19	199	200
20	189	184
21	177	176

### Reagents

**0.05 *N* CERATE REAGENT.** Dissolve 14.5 grams of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  in 500 ml. of 2 *M* perchloric acid and heat in a boiling water bath for 2 hours. Cool, let stand for 2 days, and standardize against ferrous ammonium sulfate solution.

**0.02 *N* FERROUS AMMONIUM SULFATE.** Dissolve 8 grams of ferrous ammonium sulfate hexahydrate in 1 liter of 0.36 *N* sulfuric acid solution. Standardize against a standard solution of potassium permanganate.

**8-HYDROXYQUINOLINE REAGENT.** Dissolve 1 gram of 8-hydroxyquinoline in a solution containing 89 ml. of absolute ethyl alcohol, 10 ml. of concentrated ammonium hydroxide, and 1 ml. of concentrated hydrochloric acid. Make up a fresh solution every 4 or 5 days.

The cerate reagent is not particularly stable and, if it is not prepared carefully, it loses strength very rapidly. It was found that, if the salt was dissolved in the acid solution and immediately standardized, there was a day by day decrease in normality, and that when the reagent was prepared and then heated in a boiling water bath for 30 minutes and allowed to stand for 48 hours before standardization, the day by day decrease in normality was smaller. The normality of one bottle of reagent prepared this way decreased 4 per cent in 2 weeks. Heating for 2 hours followed by 48 hours' standing resulted in a 5.5 per cent decrease in titer during the heating period but no measurable change during the subsequent 2 weeks after heating.

When the reagent is prepared with a normality less than 0.05, the loss in titer with standing is greater. A 0.05 *N* sample was prepared and heated for 30 minutes. After standing for 2 days, an aliquot was diluted to 0.005 *N* and the day by day decrease in titer studied. A 15 per cent loss in normality was observed to occur in 7 days.

During the heating period the reagent becomes cloudy, because of the formation of a fine white precipitate, which takes about 48 hours to settle. After settling, the clear solution may be transferred by siphoning to another bottle or it may be pipetted from the original bottle, as needed, if care is taken not to disturb the precipitate.

The perchloric acid should be added to the water before attempting to dissolve the hexanitrate cerate, since this reagent tends to precipitate out, in low as well as in highly acid solutions.

### Procedure for Biological Materials

Weigh out a sample large enough to contain not less than 0.05 mg. and not more than 3.00 mg. of magnesium calculated as the oxide. Place in a platinum dish, add 1 ml. of concentrated sulfuric acid, and mix well. Evaporate on a steam bath to dryness and ash in a muffle held between 500° and 600° C. When the ash is white, remove from the muffle.

Dissolve with a few milliliters of 6 *N* nitric acid, transfer to a beaker, and evaporate to dryness. This step may be left

out if the product does not contain tin. Warm the sample with 1 ml. of concentrated hydrochloric acid, dilute with several volumes of water, and filter out the tin and silica. Traces of tin may dissolve again in the hydrochloric acid but will be removed along with the iron and aluminum. Add a few drops of bromine water to the filtrate to oxidize the iron, boil to remove excess bromine, and bring to a pH of approximately 4.0 with dilute sodium hydroxide, using bromocresol green as an indicator. Make the final adjustment of the pH with 20 per cent sodium acetate. A slight excess of phosphate is necessary to precipitate the iron at this pH. Filter out the iron while hot and wash with distilled water. Add 1 ml. of saturated sodium oxalate solution, bring to pH 4.4 to 4.6 with a solution of dilute oxalic acid, heat to boiling, cool, and let stand for 2 to 3 hours to allow precipitation of the calcium. Filter and wash with ammonia water (1 to 50).

Bring the solution to a yellow shade with dilute hydrochloric acid. Evaporate the filtrate to approximately 10 ml., cool, and add 5 ml. of the 8-hydroxyquinoline reagent. Place a watch glass over the beaker and hold at a temperature just below boiling for 15 minutes. Cool and filter, using a sintered-glass filter stick (5, 6) having a thin layer of asbestos over the filtering disk. Wash the beaker once with 95 per cent alcohol and then six to eight times with 1 *N* ammonia. Make sure that all the alcohol has been washed out of the beaker, since it interferes in the final determination. Dissolve the precipitate in the beaker and on the filter stick with 5 ml. of 2 *M* perchloric acid and make up to such a volume that a 5-ml. aliquot contains between 0.05 and 0.10 mg. of magnesium oxide. Add 5 ml. of cerate reagent to the above aliquot and heat in a water bath held between 96° and 100° C. for 10 minutes. Cool and titrate the excess cerate with standard ferrous ammonium sulfate solution, using *o*-phenanthroline ferrous sulfate as an indicator. Calculate the per cent of magnesium, assuming that 59.7 equivalents of cerate reagent are used per mole of magnesium.

Known quantities of magnesium were determined by the third part of the above procedure in order to calculate the exact value of the oxidation factor. Table II shows that the precipitation and oxidation are reproducible. The oxidation factor calculated from the data in Table II amounts to 59.7 equivalents of cerate per mole of magnesium.

At the time this method was being developed, the ash of canned tomatoes was being analyzed in the laboratory and, therefore, samples of this product were selected to check the procedure. It was believed that the difficulties encountered in the analysis of canned tomatoes would be representative of those met with in any ashed biological material. These samples also contained added iron, which interferes if not removed. A duplicate determination was made by another analyst, using the method of the Association of Official Agricultural Chemists (1). Good agreement was obtained between the two methods, as is shown in Table III.

### Discussion

In the earlier stages of this work magnesium quinolate was filtered through a sintered-glass Gooch crucible. This



procedure was abandoned in favor of the filter-stick filtration because of the high blank obtained by the former method. Either efficient washing was not obtained or traces of contamination were introduced with the use of the Gooch crucible. The filter sticks are easily made by the method described by Stone and Weiss (6) or Kirk (5). The asbestos used over the end of the filtering disk was previously soaked in concentrated nitric acid to oxidize any organic material which might be present.

With this procedure several other determinations can be made on the same ash, if a sample of suitable size is taken. In this laboratory, manganese, potassium, and calcium, as well as magnesium, were all determined on the same sample.

### Summary

An oxidation method for the determination of magnesium by precipitation with 8-hydroxyquinoline and oxidation of the precipitate with ammonium hexanitrate cerate is proposed.

The principal advantages of the method are the elimination of the bromination procedure of the other 8-hydroxy-

quinoline methods and its very large factor, amounting to 59.7 equivalents of oxidizing agent per mole of magnesium.

Excellent agreement of the results between this method and the A. O. A. C. tentative method was obtained on twenty-one samples of canned tomatoes analyzed by both methods by different analysts.

### Acknowledgment

The author wishes to acknowledge the assistance of H. C. Stoner, who carried out the analyses for magnesium by the A. O. A. C. tentative method.

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# Partition of the Less Easily Digested Carbohydrate Complex of Forages

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IN DIGESTIBILITY and metabolism experiments it has been the custom to analyze the feed and feces for crude fiber and then obtain nitrogen-free extract by difference. This method of partition of the carbohydrate components of feed stuffs is an empirical one and is not entirely satisfactory, especially for the more exacting problems. The usual crude-fiber method, the so-called Weende method as proposed by Henneberg, has been in general use with only minor alterations since 1864.

Both enzymatic and chemical methods have been applied to the problem of separating the less easily digested carbohydrate components generally spoken of as crude fiber. In the enzymatic methods pepsin, diastase, trypsin, and pancreatin alone and in different combinations have been used to obtain the undigested residue of the diet. Chemical methods have been used to determine the amounts of lignin, cellulose, hemicellulose, and other materials present in the sample under investigation. While these methods are not entirely satisfactory, they possess certain advantages over the older official method for crude fiber.

Williams and Olmsted (5) used pancreatin digestion as a preliminary treatment before the determination of lignin. Horwitt, Cowgill, and Mendel (2) used pepsin, diastase, and trypsin digestion. Crampton and Maynard (1) used pepsin digestion before determination of lignin. Norman (3) extracted and hydrolyzed the sample before the lignin determination. The lignin method most generally used involves the use of 72 per cent sulfuric acid by weight.

In certain digestibility studies on forage crops a method was required which would yield information that could not be obtained by the usual method, and would be sufficiently simple to be readily adapted to routine laboratory procedure. A number of methods were tried, modifications were introduced, and finally from these studies a method was devised which seems to have a number of advantages over former methods when applied to the problems under investigation.

### Experimental

The method described in this paper is a combination of enzymatic and chemical procedures and involves several modifications of the methods mentioned above. A preliminary extraction of the sample with dry ether before treatment with enzymes has been found very helpful in obtaining more uniform enzymatic action, especially with grasses. It has also been found necessary to autoclave the samples before adding the enzymes to prevent the growth of molds.

The methods proposed by Williams and Olmsted and by Horwitt, Cowgill, and Mendel were used on a sample of red-top grass which was cut in early June. The Williams and Olmsted method gave higher results for the undigested residue than the Horwitt, Cowgill, and Mendel method, but approximately the same results on samples of feces.

The effectiveness of various treatments in removing nitrogen from a sample of redtop was tested and the results, given in Table I, showed that enzymatic digestion was the most effective treatment for the removal of nitrogen from the grass. In subsequent work it was adopted for preliminary treatment of the sample. The Horwitt, Cowgill, and Mendel method was modified by using a smaller volume and reducing the amount of pepsin and trypsin. It was found that the amount of pepsin and trypsin did not have a pronounced effect on the amount of nitrogen removed from the sample if more than 50 mg. per gram of sample were present. The trypsin extract should be filtered before use to prevent any undissolved material from increasing the weight of the residue.

Tests on fineness of grinding of the grass showed best results when the entire sample passed through a 0.5-mm. screen. Apparently, the enzymatic action is more uniform if the particles are small, and the amount of material digested is greater in fine than in coarse samples.

After the enzymes have digested the sample, the next



TABLE I. EFFECT OF TREATMENT ON AMOUNT OF PROTEIN LEFT IN RESIDUES FROM REDTOP GRASS

Treatment	Crude Protein (Nitrogen × 6.25) in Residues
	%
None (original grass)	11.75
Alcohol-benzene extraction	11.46
5% H <sub>2</sub> SO <sub>4</sub> , 1 hour	5.53
Norman's procedure (lignin)	4.17
0.1 N HCl without enzymes, 24 hours	3.50
Water, 96 hours	3.25
Enzymes	2.50

TABLE II. INFLUENCE OF FORMALDEHYDE IN CRAMPTON-MAYNARD METHOD ON YIELDS OF LIGNIN IN GRASSES

Sample	Lignin Yield		
	Original method	Modified Method Without HCHO	Excess HCHO
	%	%	%
Redtop (cut June 3)	7.31	6.10	8.52
Redtop (cut June 20)	11.97	9.63	..
Centipede (from Fla.)	11.64	10.42	14.16
Centipede (from Ga.)	11.20	9.34	13.12

step is the determination of the lignin. The concentration of the acid is an important factor. The results showed that for grasses the concentration must be above 65 per cent by weight; below this the results are too high.

The time and temperature factors of the 72 per cent acid method have been studied by Ritter, Seborg, and Mitchell (4). The results that they obtained using wood were confirmed in the present experiments on grass.

Formaldehyde (1) has been used to bring about quicker solution of the sample and to improve the rate of filtration. Its use was found to increase the yield of lignin. Accordingly, the method of Crampton and Maynard (1) was modified by varying the amount of formaldehyde. Results of this modification are given in Table II.

It is evident that formaldehyde does increase the apparent lignin content of grass. It is believed that an insoluble compound results from the action of formaldehyde on some component of the grass, with the probable formation of a resin.

In order to adapt the method to a routine procedure that would handle a large number of samples, it was desirable to eliminate the long reaction time at low temperatures. The method was modified so that the reaction could be carried out at room temperature. The reaction vessel with the sample was placed in a freezing bath and cooled before the addition of the sulfuric acid. The acid was chilled and added in small portions with constant stirring. The sample was removed from the freezing bath at the end of 15 minutes and allowed to stand at room temperature for about an hour, being stirred frequently during the entire reaction period. This procedure kept the temperature well below 30° C. and prevented any charring of the sample. Table III shows the effect of time on the reaction.

A number of samples of grasses and legumes were analyzed by the method outlined in this paper and by the method of Norman (Table IV). The differences between the two methods are probably due to the protein left in the lignin fraction, since it is known that protein interferes with the determination of lignin. The figures indicate that treatment with enzymes in the proposed method removes more protein from the sample than the extraction method used by Norman.

**Outline of Proposed Method**

Extract 1-gram sample with anhydrous ether for 16 hours, transfer the dried extracted sample to a 100-ml. wide-mouthed glass-stoppered bottle, and moisten with distilled water. Auto-

clave the sample at 18 pounds' pressure for 1 hour. Cool, add 50 ml. of 0.1 N hydrochloric acid and 0.1 gram of pepsin (1 to 3000), and incubate at 40° C. for 48 hours. Shake occasionally during the incubation period. Neutralize with sodium hydroxide and adjust to pH 4.5 with hydrochloric acid. Add 0.1 gram of clarase and incubate for 48 hours. Filter and wash residue with water. Return residue to bottle, and add 60 ml. of an aqueous extract of trypsin made up to contain 0.1 gram of trypsin powder. Make solution slightly alkaline with sodium hydroxide and incubate 96 hours. Filter and wash the residue with water, alcohol, and ether. Dry at 110° C. for 1 to 2 hours and weigh. Report as undigested residue. Make all filtrations through 200-mesh bolting silk. Transfer the residue to aluminum moisture dishes for final drying and weighing.

Hydrolyze the undigested residue with sulfuric acid (5 per cent by weight) for 1 hour, filter, and wash residue with hot water and finally with alcohol. Dry, transfer to a 100-ml. beaker, place in a freezing bath, and add slowly 20 ml. of sulfuric acid, (72 per cent by weight) with constant stirring. After 15 minutes remove from freezing bath and allow reaction to continue at room temperature for 45 to 60 minutes. The mixture must be stirred during the reaction period. Transfer to a 1-liter Erlenmeyer flask, dilute to 3 per cent acid by weight, and reflux for 2 hours. Filter and wash residue with hot water. Dry at 110° C., weigh, ignite, and reweigh. Report loss of weight as lignin.

The final filtration should be carried out within 30 minutes after the completion of the refluxing. If the solution is allowed to become cold, it is hard to filter and wash. A sample that filters slowly and is difficult to wash will be high and should be discarded.

**TABLE III. INFLUENCE OF TIME OF REACTION ON YIELDS OF LIGNIN**

Time Min.	Lignin in Grasses		
	Centipede (Fla.) %	Centipede (Ga.) %	Redtop %
45	8.45	7.51	8.02
50	8.30	7.45	..
55	8.30	6.80	7.21
60	8.08	6.82	5.96
75	8.23	7.31	6.14
90	8.55	7.20	6.47
105	8.47	7.48	..

**TABLE IV. COMPARATIVE YIELDS OF LIGNIN BY NORMAN AND PROPOSED METHODS**

Sample	Date of Cutting	Lignin Yield	
		Proposed method %	Norman method %
White clover	3 inches high	8.22	10.68
White clover hay	.....	9.02	11.15
Kentucky bluegrass	August 1	10.10	12.00
Kentucky bluegrass	September 3	9.34	10.85
Orchard grass	May 23	5.60	8.86
Orchard grass	June 16	8.88	10.66
Alfalfa	September 21	9.66	12.55
Alfalfa leaf meal	.....	7.17	10.38
Redtop	June 3	6.24	6.22
Redtop	June 20	6.88	8.19
Centipede grass from Fla.	September 2	8.37	8.04
Centipede grass from Ga.	September 2	7.41	7.02

A satisfactory determination of cellulose was obtained by the acetic acid-nitric acid method of Kürschner and Hanak, which was also used by Crampton and Maynard (1). The sum of the lignin and cellulose thus obtained is usually considerably less than the undigested residue obtained by enzymatic digestion. Thus far no attempt has been made to separate or study the remaining undigested material obtained by difference.

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# Automatic Effusimeter for Determination of Specific Gravity of Gases

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An automatic effusimeter has been developed which is considered more accurate than the regular manually operated type. It eliminates personal error in handling a stop watch, and gives results which are very reproducible and accurate.

THE specific gravity of gases is usually expressed as the ratio of the weight of a given volume of the gas to the weight of an equal volume of air, both measured under the same conditions of temperature and pressure. However, the method of direct weighing is not well adapted to routine testing as practiced in the various branches of the petroleum industry; so when a large number of determinations is required, comparison methods are almost universally employed. The comparison methods fall into two classes: (1) effusion methods, and (2) indirect weighing methods.

Since the author has had extensive use for the effusion method, work has been done to improve its accuracy, particularly with respect to timing. The effusion method is based upon the fact that the times required for the flow of equal volumes of two gases through the same orifice are approximately proportional to the square root of their specific gravities. The specific gravity thus can be calculated from the following equation:

$$\frac{\text{Sp. gr. of gas}}{\text{Sp. gr. of air}} = \frac{t^2 \text{ gas}}{t^2 \text{ air}}$$

If the specific gravity of air is taken as unity, then

$$\text{Sp. gr. of gas} = \frac{t^2 \text{ gas}}{t^2 \text{ air}}$$

where  $t$  is the time in seconds required for the flow of a given volume of the gas or air.

Edwards (2) has made an extensive investigation of the accuracy of the effusion method and found that although no results of high accuracy can be expected from apparatus of the effusion type, yet it should serve well for approximate results, or for control work where relative values only are needed. He also pointed out that by the observance of certain precautions in the construction and use of the apparatus, it is possible to secure results accurate to about 2 per cent. Greater accuracy and reliability can be obtained by standardizing the apparatus.

The method, because of the relative simplicity of the apparatus originally designed by Bunsen (1) and later improved by Schilling (3), is widely used.

## Regular Effusimeter

The apparatus consists of a glass cylinder 3.5 inches in diameter by 12 inches deep with a metal top plate. An armored glass tube extends through the metal cover from the top and almost to the bottom of the cylinder, which is filled with water. Attached to the glass tube is a three-way brass stopcock which contains a glass tip. The tip itself contains a small platinum disk with a standardized orifice.

This apparatus finds wide application in the routine testing of the specific gravity of gases, particularly in refineries and plants in locations which are too small for practical use of larger assemblies of apparatus.

It is generally recognized that when water is used as a confining fluid, some of the difficulties encountered in obtaining accurate results may be attributed to the condensation of moisture on the edges of the orifice. The solubility of the gases in water also has some effect. Mercury, on the other hand, does not possess these disadvantages, since its vapor pressure is negligible, and as far as solubility is concerned, the only trouble encountered is due to hydrogen sulfide. However, even with mercury as a confining fluid, it is still difficult to obtain reproducible results, because of the error in timing. A considerable error in this regard may be introduced if the eye is not kept on the same level with the graduation at the time of starting or stopping the stop watch. In order to eliminate an error from this source, an effusimeter containing an automatic timing system has been built and is herewith described.

## Automatic Effusimeter

The apparatus, as constructed, is essentially a modification of the conventional design using mercury as a displacing medium. The general arrangement of the apparatus is shown in Figure 1.

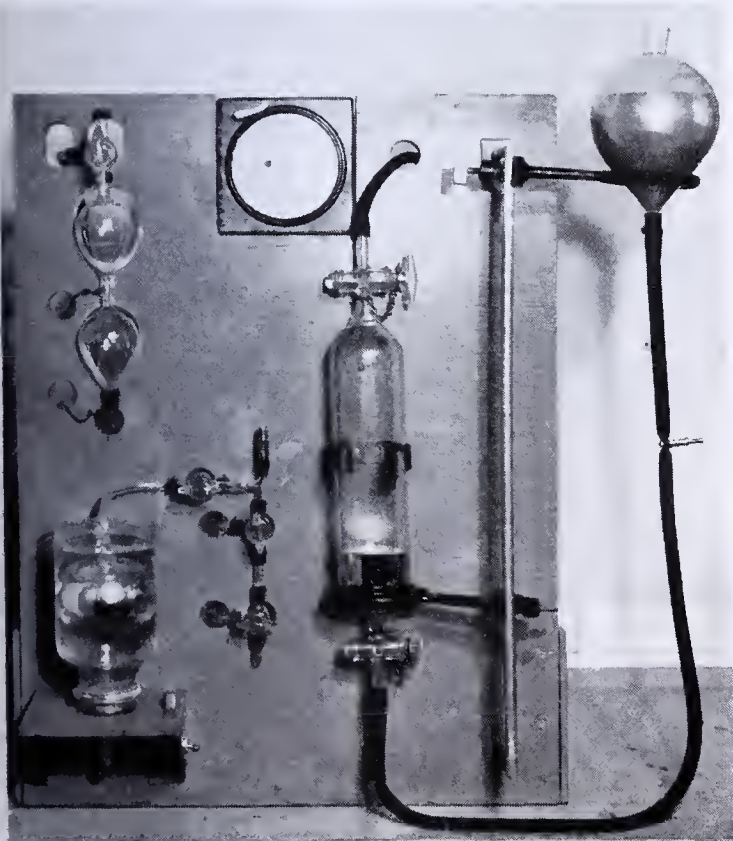


FIGURE 1



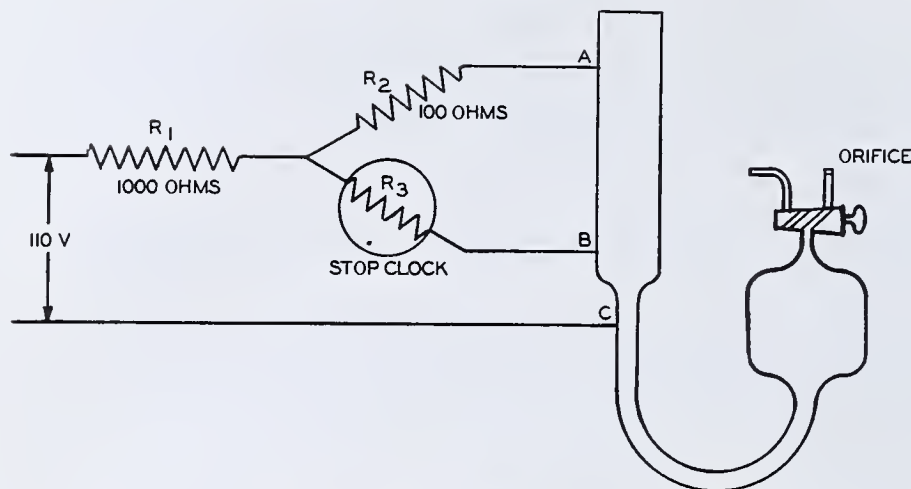


FIGURE 2. TIMING CIRCUIT

The gas chamber surrounded with a water jacket is sealed to a two-way stopcock. One way leads to the orifice and another serves to receive a gas sample from the sample tube. A drying tube containing calcium chloride is used to remove moisture from the gas sample, and is located at the back of the equipment, and so is invisible in Figure 1. The mercury reservoir is made of either two pear-shaped bulbs or a straight cylindrical form.

When a sample is introduced into the gas chamber it displaces mercury from the latter into the mercury reservoir, which has three electrical contacts sealed through its wall. An electric stop clock is connected to the contacts as described below; as long as the mercury covers all three contacts the stop clock does not run. The stopcock is opened to the orifice, the gas begins to escape, and the column of mercury in the reservoir begins to descend. At the instant the mercury passes the upper contact, the stop clock is started and continues to run until the middle contact is passed. This stops the clock. Reading of the clock then gives time of efflux in hundredths of a second if desired.

### Timing System

In designing the automatic timing system it was desirable to avoid use of a relay. It was evident that this would increase the cost of the apparatus and at the same time would require more servicing and replacement. The problem was solved by utilizing the principle of the series-parallel circuit.

The circuit as constructed consists of two parallel resistances  $R_2$  and  $R_3$ , in series with a line resistance,  $R_1$ , as shown in Figure 2. In the parallel circuit of two resistances  $R_2$  and  $R_3$ , the currents are inversely as the resistances:

$$\frac{I_2}{I_3} = \frac{R_3}{R_2}$$

The current in each branch may be represented as follows:

$$I_2 = \frac{E}{R_2}$$

$$I_3 = \frac{E}{R_3}$$

$R_3$  is resistance of the stop clock and has therefore fixed value. With  $R_2$  less than  $R_3$  more current flows through  $R_2$ . By selecting a proper value for  $R_2$  it is possible to reduce  $I_3$  to such an extent that the stop clock will not run when all contacts, A, B, and C, are submerged in mercury. Then, as the contact, made through the mercury, is broken at A, all the current becomes available for  $R_3$ —i. e., to start the clock. Breaking of the circuit at B then stops the clock.

Wire-wound resistors are used, for they are completely coated with a vitreous porcelain enamel which protects the windings against moisture and mechanical injury.

The stop clock used is obtained from the Standard Electric Time Company, Springfield, Mass. It has a magnetic starter.

The timing system is different from one described by Edwards (2) in two respects: (1) Instead of a chronograph, an electrical stop clock is used, thus eliminating use of graph paper; and (2) the platinum contacts are not situated within

the gas chamber but inside a mercury reservoir which is open to the air. If the electrical contacts were placed within the gas chamber there would be a potential danger of explosion with some gases under test. Explosive mixtures can be formed in case of incomplete flushing, or the sample itself may be ignited by an electric spark produced at the moment contact is made. By placing the contacts in a mercury reservoir, the apparatus is safe to use even when the gas being tested is within the limits of explosibility.

The obvious advantage of the automatic timing system is the fact that it eliminates error in timing due to the human factor, and at the same time makes the determinations less tedious to perform.

### Results

As a part of this investigation a series of tests was made on several samples of gas in addition to air which served as a standard. The time of efflux was found to be easily reproducible. This reproducibility in timing allows for good checking even when determining specific gravity to the third significant figure. Results obtained are as follows, air being used as standard:

Gas	Effusimeter	Balloon Method	Deviation %
Commercial $H_2$	0.0850	0.0824	+3.2
Manufactured $H_2$	0.1290	0.1243	+3.8
$H_2 + CH_4$	0.3467	0.3444	+0.7
$CH_4 + C_2H_6$	0.678	0.660	+2.7
$N_2 + CH_4$	0.842	0.843	-0.1

Each determination consisted of several runs on the test gas, preceded and followed by several runs on air. The number of runs in each determination was usually from three to five.

Results by the balloon method represent single determinations. It is not to be expected that the balloon method values will check the effusimeter ones, because of the different principles involved in the two tests. The time of efflux is reproducible within 0.2 second and usually within 0.1 second.

#### Examples of Actual Runs

1. 55.85, 55.88, 55.88 seconds
2. 46.94, 46.84, 46.86, 46.89, 46.91 seconds
3. 56.09, 56.09, 56.12, 56.19, 56.02, 56.12 seconds
4. 19.76, 19.76, 19.80, 19.73, 19.70 seconds

Table I shows how a variation of 0.1 to 0.2 second affects value of the specific gravity of different gases (calculated).

TABLE I. EFFECT OF VARIATION IN TIME

Time of Efflux for Air Sec.	Time of Efflux for Gas				
	15 Sec.	30 Sec.	45 Sec.	60 Sec.	75 Sec.
	Specific Gravity				
54.5	0.0758	0.303	0.682	1.211	1.893
54.6	0.0755	0.302	0.679	1.207	1.886
54.7	0.0753	0.301	0.677	1.203	1.881

This automatic effusimeter is recommended for routine determinations of the specific gravity of gases, except those containing hydrogen sulfide.

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# Capillary Flowmeter with Variable Orifices

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IT IS well known that wherever any degree of accuracy is desired, the conventional capillary flowmeter is limited to a relatively narrow range of gas flows, depending upon the diameter and length of the capillary tube used. Hence it has been customary in many laboratories to use flowmeters provided with interchangeable capillaries, each of which may be attached to the flowmeter by means of one or two ground joints.

Ever since the introduction of modern manufacturing methods for the production of corrosion-resisting alloy wires

such as chrome-nickel, Chromel, etc., diameters have been more rigidly observed, with much smaller tolerances allowed, than in specifications for ordinary glass capillary tubing. It was felt that advantage should be taken of this fact in the construction of variable orifices.

In the new type of flowmeter shown in Figure 1, the vertical capillary tube should be designed for the maximum gas flow expected. Wherever the flowmeter is to be used accurately for lower gas rates, the orifice is decreased by inserting a wire of suitable gage into the entire length of the glass capillary. Thus a different calibration curve will be obtained for every size of wire used.

TABLE I. RELATION BETWEEN GAS FLOWS AND PRESSURE DIFFERENCE FOR VARIOUS WIRE SIZES

B. and S. Gage Wire Used in 60 × 1.1 Mm. Glass Capillary	Approximate Gas Flow		
	10 mm. Hg	60 mm. Hg	100 mm. Hg
	Liters per minute		
20	0.2	0.7	1.1
21	0.3	1.2	1.7
22	0.4	1.7	2.6
23	0.5	2.1	3.0
24	0.6	2.4	3.5
25	0.7	2.7	3.9
26	0.8	2.9	4.2
27	0.9	3.1	4.3
29	1.0	3.3	4.7
30	1.1	3.6	5.0
None	1.5	4.8	6.5

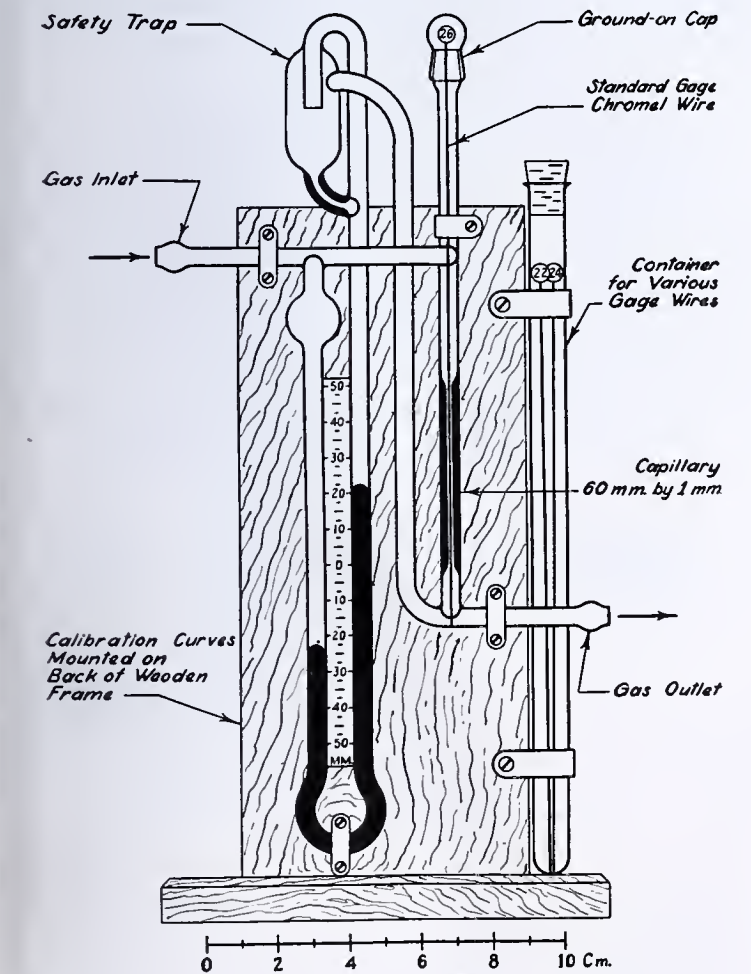


FIGURE 1. FLOWMETER

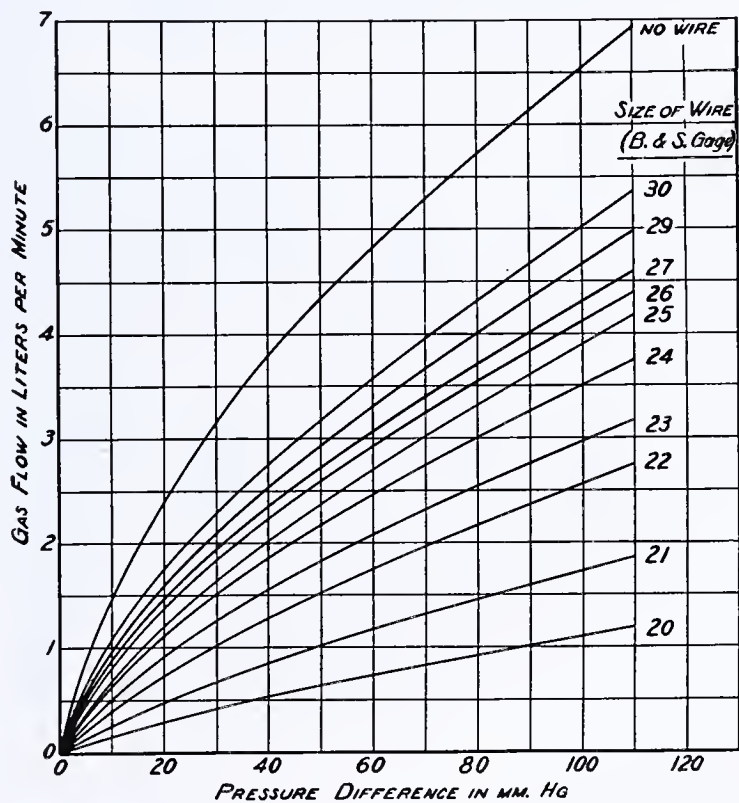


FIGURE 2. CALIBRATION CURVES

By using wires of different sizes, a flowmeter having a capillary 60 mm. long and 1.1 mm. in diameter can be used for accurate measurements of gas flow covering the complete range between 0.2 and 7.0 liters per minute. The calibration curves are shown in Figure 2, and the approximate ranges of gas flows to which each wire is applicable when used in a capillary tube 60 × 1.1 mm. are tabulated in Table I.

While most flowmeters designed for low flow rates contain small capillaries which sometimes are difficult to clean, the new flowmeter is readily cleaned by removing the inserted wire. During one year's use, the flowmeter has been found very convenient in every respect and no variations have been noted in the calibration curves during this time.

## Acknowledgment

For the assistance rendered in the calibration of the flowmeter, the author is indebted to Francis H. Murphy of this division.



# A Mechanically Operated Continuous Liquid-Extraction Apparatus

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A modified Widmark extraction apparatus is constructed from two Erlenmeyer flasks connected side by side with a short length of wide-bore tubing sealed into the sloping walls of the flasks. The apparatus is rocked through an angle of  $\pm 15^\circ$  around an axis placed beneath the horizontal connecting tube. A plant extract acidified to pH 1.0 is placed in one flask and 0.5 N sodium bicarbonate in the other; ethyl

acetate is then added to the level of the connecting tube. As the solvent flows back and forth during oscillation, the organic acids are gradually collected in the alkali. The apparatus may be used in small sizes for quantitative analytical extractions and in larger sizes for preparation work. It can be applied equally well for the extraction of such basic substances as nicotine.

FOR the quantitative removal of such substances as organic acids or nicotine from extracts of tobacco leaf tissues, a simple modification of the Widmark extraction apparatus (2) has proved to be exceedingly efficient and doubtless may have many other applications. The device possesses the advantage of offering no fire hazard and can be constructed in sizes suitable for the extraction of aqueous volumes of from 10 ml. to several liters at one time.

The apparatus consists of two equal Erlenmeyer flasks joined closely side by side with a short straight wide-bore tube sealed horizontally into the sloping walls of the flasks somewhat more than one third of the distance up from the bottom. The pair of flasks is mounted on a platform that can be rocked through an angle of about  $\pm 15^\circ$  from the horizontal around an axis of rotation placed vertically beneath the connecting tube and at right angles to it. One of the flasks is charged with a volume of the acidified aqueous solution to be extracted such that, when the platform is tilted to the maximum angle, there is no danger that any of it will run through the connecting tube into the second flask. The second flask is charged with a similar volume of sodium bicarbonate solution, and organic solvent is then poured in, with the platform level, until it reaches the connecting tube.

The flasks are lightly stoppered and the motor that drives the oscillating platform is started; solvent flows alternately back and forth, each time carrying a small amount of organic acid extracted from the acidified solution and giving it up to the aqueous alkali. The gentle agitation, as the solvent pours from side to side, gives sufficient mixing with the aqueous fluid with little or no danger of froth formation, and ultimately transfers all of the extractable acid to the alkaline solution. The apparatus can be allowed to run without attention save for an occasional check to see if water is migrating from one side to the other, as may happen unless the two aqueous solutions are approximately isotonic. At the end of the extraction period, the two aqueous solutions are separately withdrawn from beneath the solvent by suction through a suitable pipet into a receiving flask, a minimal amount of wash water is placed in the flasks, agitated a few times, and withdrawn, and the apparatus is ready for the extraction of a further charge without removal of the solvent.

Table I shows the dimensions of three sets of flasks that have been used successfully in this laboratory for several years. The smallest, constructed from 500-ml. wide-mouthed Erlenmeyer flasks, is employed for the quantitative extractions required in certain analytical methods; the larger sizes, made from ordinary Erlenmeyer flasks, are used for preparations.

The oscillating platform is bolted with suitable brackets on the beam of a discarded two-cylinder Geryk vacuum pump from which the pump mechanism had been removed. The flywheel (44.5 cm., 17.8 inches in diameter) is driven by a belt from a

pulley mounted on a reduction gear of the ratio 190 to 1 which is in turn driven by a 0.25-horsepower motor that turns at 1725 r. p. m. The exact speed of rocking is controlled by the size of the pulley on the reduction gear. With the authors' apparatus, a 10-cm. (4-inch) pulley gives about 2 complete cycles of extraction per minute, which is unnecessarily slow, and a 12.5-cm. (5-inch) pulley gives about 2.7, which is a little too fast. The most satisfactory adjustment can easily be made by building up the diameter of a 10-cm. (4-inch) pulley with rubber bands cut from the inner tube of an automobile tire.

The platform for the large extractors carries two of these side by side and is furnished with a deep-sided pan fitted with a drain that discharges through rubber tubing into a bottle to provide against accidental breakage. The flasks fit into spring clips soldered to this pan, so that they are held securely in position. The platform for the small extractors carries four or more, which do not need to be mounted exactly over the axis of rotation.

## Choice of Solvent

Tests of the apparatus were made with a solution of citric acid, which has been found the most difficult to extract of any of the common plant acids. Observations on extracts from tobacco leaf tissue showed that 10 days' continuous operation with ether as solvent removed only 90 per cent of this acid from 3-liter samples of extract in the largest extractors, and a search was therefore made for a more efficient solvent. Data in Table II show that ethyl acetate

TABLE I. DIMENSIONS OF EXTRACTION APPARATUS

Charge of Aqueous Solution Liters	Volume of Erlenmeyer Flask Liters	Diameter of Connecting Tube Cm.	Vertical Distance from Bottom of Connecting Tube to Bottom of Flask Cm.	Horizontal Distance between Flasks at Bottom Cm.
0.01 to 0.05	0.5	2	3.5 to 3.8	3 to 3.5
0.5 to 1.0	3	3.5	11	5 to 8
2.5 to 3.0	6	6	14	10 to 12

TABLE II. EXTRACTION OF CITRIC ACID WITH VARIOUS SOLVENTS

(Apparatus oscillated to give 144 extractions per hour)

Solvent	Citric Acid Taken Gram	Volume of Aqueous Solution Ml.	Extraction Time Hours	Recovery %
Ether	0.032	40	29	34.0
Methyl amyl ketone	0.032	40	23	33.0
Amyl acetate	0.032	40	46	81.0
Isopropyl acetate	0.032	40	24	90.0
Ethyl acetate	0.032	40	17 to 24	95.0 to 98.0



is the most advantageous of those tried and may be relied upon to bring about nearly quantitative extraction in about 24 hours. Malic and oxalic acids, as well as the small proportion of unknown acids in tobacco leaf extracts, are somewhat more readily extracted.

In preparation for extraction, the aqueous solution is brought to pH 1.0 by the addition of sufficient sulfuric acid. The alkali solution usually employed is 0.5 *N* sodium bicarbonate. Ethyl acetate possesses the disadvantage of undergoing slight hydrolysis with a corresponding accumulation of acetate in the alkaline extract. Accordingly extracts prepared in this way cannot be used for organic acid titrations (1).

The acidity to which the solution on the acid side is adjusted must be carefully controlled. Oxalic acid is incompletely extracted unless the reaction is close to pH 1.0, but a high acidity is to be avoided because of the danger of hydrolyzing excessive amounts of ethyl acetate.

Nitric acid, if present in the tissue extract, is likewise quantitatively extracted along with the organic acids, when the reaction is adjusted to pH 1.0, but extraction is incom-

plete at pH 1.5 in 22 hours on samples in the small apparatus. Extraction by this technique therefore provides a convenient method for removing nitric acid from a plant extract if subsequent investigation of organic nitrogenous substances is contemplated.

The large extractors have also been of service in the isolation of nicotine. Benzene or ether may be used as solvent, the tissue extract is made strongly alkaline to phenolphthalein, and the nicotine is absorbed in 0.5 *N* sulfuric acid. In one preparation, 5 liters of extract were treated simultaneously in two large extractors. Of the 200 grams of nicotine present, 95 per cent had been removed in 24 hours at the usual oscillation rate of 144 extractions per hour.

The application of the small extractors to the quantitative removal of pyrrolidone carboxylic acid forms one step in a new method to determine glutamine, to be described in another paper.

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## Lead-Sodium Alloy as a Drying Agent

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LEAD-sodium alloy has been used in this laboratory for several years in place of metallic sodium for drying inflammable liquids such as ether because it is less hazardous to handle. Fires occasionally occur in the handling of fresh

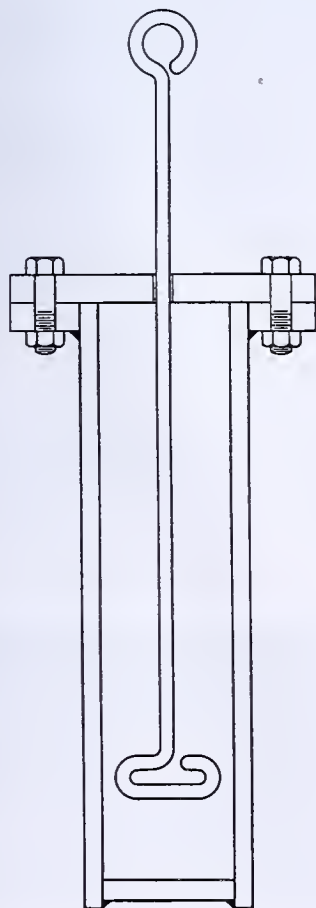
metallic sodium and in the disposal of incompletely reacted metal in contact with inflammable liquids or vapors. Lead-sodium alloy reacts only slowly with air or water, yet dries ether as completely as sodium wire. Furthermore, the residues of ether or other liquids still containing some active alloy can safely be destroyed by the addition of water, as the reaction never reaches the violence observed in the case of the metal itself. The alloy is very brittle and can, therefore, be prepared in any desired state of subdivision much more conveniently than in the case of sodium wire.

The reactivity of sodium in this form also suggests that the alloy might well be considered as a substitute for pure sodium in chemical reactions wherever the presence of lead is not objectionable and where the extreme state of subdivision which can readily be obtained with the alloy is of material interest.

### Preparation of Alloy

An iron crucible is fitted with a lid through which is passed a stout iron wire which should be used as a stirrer as shown in the diagram. The crucible is filled with 90 parts of lead and 10.5 parts of sodium and the lid is inserted. These proportions are selected to give NaPb as the product, because this sodium concentration is the lowest and safest which still provides an active, brittle material.

The crucible is heated on a flame or in an electric furnace until the mass is liquid, at which time the stirrer is operated for a few minutes. The crucible is then tipped at an angle of approximately 45° and allowed to cool, after which its contents are readily removed by inverting and hammering lightly on the side and bottom. The alloy falls out in brittle lumps which can be transferred at once to an air-tight container for storage. Whenever alloy is needed for use, an appropriate amount is removed from the container, broken into small lumps in a mortar, and quickly poured into the liquid to be dried. If more rapid reaction is desired, the alloy may be ground to a fine powder; in this case it is advisable to effect the grinding under the liquid to be dried in order to minimize the absorption of moisture from the air. Finely ground powder, if not protected by the liquid, may react





with excess moisture from the air sufficiently to cause the alloy to burn.

Upon reaction with water, the alloy disintegrates into a fine powder and the sodium is effectively used quantitatively for drying. The convenience in handling, the efficacy of use, and the safety and ease of disposal of the residues more than offset the seeming drawback of handling a large amount of otherwise inert metallic lead.

The alloy, NaPb, is made industrially as an intermediate in the manufacture of tetraethyllead and is particularly easy to manufacture on a semiworks scale.

It would seem, therefore, that if the demand would justify its production on a larger scale, it would be an easy matter for the supply houses to stock the alloy and sell it at a price which could compete with that of metallic sodium on the basis of available sodium.

## Small Centrifuge Tube Filter

THEODORE PERRINE AND WILLIAM KUMP

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WHEN working with relatively small amounts of substances using centrifuge technique, separation of solid material from liquid is sometimes troublesome, particularly when the solid has approximately the same specific gravity as the liquid. It is also often desirable to separate solid from liquid as rapidly as possible, as when working at low or high temperatures.

Various methods have been used to overcome these difficulties. The Skau tubes (2) have the advantage of being completely closed, so that it is possible to work under anhydrous conditions, but they are expensive and perhaps not so convenient to handle as the ordinary 15-ml. centrifuge tube. The tube proposed by Cheronis (1), while very inexpensive, has the disadvantage of having a rubber stopper in contact with the liquid.

The filter described in this paper has several advantages. It is easily constructed from material which is relatively inexpensive and readily available. It conforms in dimensions to the ordinary centrifuge tube, and will, therefore, fit apparatus designed for use with centrifuge tubes. No substance but glass and filter paper comes in contact with the contents of the tube. The filter may be made moisture-proof, and may be used at low or high temperatures and without danger of contamination with outside substances.

chambers *F* and *G*. Rubber stopper *A* has a 4-mm. hole bored incompletely through the center to support stem *C* loosely. (The stopper may also be made of glass and ground in.) The holes in the filter plate may be ground through or burned through with a hot tungsten wire.

**USE.** Filter paper is cut with a cork borer to fit snugly inside the centrifuge tube, and with a small hole concentrically placed to accommodate the stem of the filter plate. Two or more such pieces of paper are slipped over the filter stem, pushed into place with a small glass rod, then moistened if desired with a little suitable solvent. The substance to be filtered is poured onto the filter, and after insertion of the stopper is centrifuged in the ordinary manner. After centrifuging, the residue on the filter is easily removed practically quantitatively by simply removing the filter from the tube, when the filter paper, if properly cut, acts as a scraper against the walls of the tube. The solvent is then removed or otherwise treated.

The filtrate may be removed through the hollow filter stem by means of a long capillary dropper, without disturbing the precipitate. If it is desired to air-dry the precipitate, suction may be applied to the filter stem.

When using the filter at above or below room temperature, the substance, the filter, and the centrifuge tube shield are all preheated or precooled. Then the substance is rapidly transferred to the filter and centrifuged. Where it is desired to maintain the air about the centrifuge tubes at a low temperature (using a centrifuge with a guard bowl), it is convenient to place finely powdered solid carbon dioxide in the bottom of the guard bowl. When the centrifuge is run, the air within the bowl is soon filled with small particles of solid carbon dioxide, and the temperature is considerably lowered in a short time.

The filter described has been used successfully to remove suspended charcoal from solutions, for the filtration of very soluble compounds, and for other uses where filtration is preferable to a centrifugal separation.

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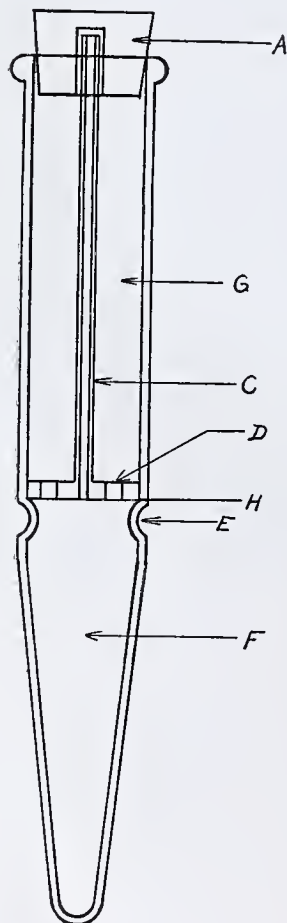
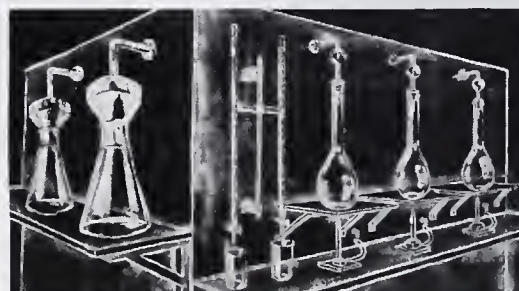


FIGURE 1

**CONSTRUCTION.** An ordinary Pyrex 15-ml. centrifuge tube is constricted at *E* as shown in Figure 1. The constriction is so placed that chamber *F* will be of only slightly smaller capacity than chamber *G*. Filter plate *D* may be made from Pyrex tubing or molded. The disk should make a snug fit inside the centrifuge tube and should be ground to a rough seat on the shoulder, *H*. Filter stem *C* is made of 3-mm. Pyrex tube to reduce weight and to permit equalization of pressure between





# A Rapid Circulating Dialyzer

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**F**REEING protein solutions or suspensions from salts is frequently a time-consuming operation, since provision is not always made for adequate stirring. Although a number of types of dialyzers have been discussed in the literature (1-4), none has all the advantages of the double continuous-flow apparatus described here.

A method for the rapid dialysis of protein solutions has been devised which combines the following advantages:

Small quantities (25 to 150 cc.) of protein solution may be 98 per cent freed of concentrated salts in 9 hours (Figure 1). This is approximately four times faster than a recently described technique (2). The method is also adaptable for larger quantities.

The construction of the dialysis apparatus permits the use of concentrated salt solutions, without danger of changing the selectively permeable character of the dialyzing membrane either by stretching or rupturing it through osmotic effects. The present technique does lead to a slight dilution of the fluid being dialyzed, which in the authors' experience has not been greater than 25 per cent even when half saturated ammonium sulfate is used.

The entire dialysis apparatus can be put into an ordinary electric refrigerator or other thermostat, and the dialysis carried out at a low or constant temperature. The washing fluid is supplied by a reservoir outside the refrigerator. The thick rubber gasket on the door of the refrigerator permits the use of slightly flattened metal tubing in order to bring fluids in or out.

The dialysis membrane (19-mm. cellophane tubing used in authors' experiments) may be used repeatedly for new samples of the same protein solution. One membrane has been in continuous use for 7 weeks without any sign of leaks or deterioration.

The solution to be dialyzed is continuously circulated by a gas pump mechanism. It is thus possible to perform the dialy-

sis in the absence of oxygen if necessary. The gas pump is so constructed as to reduce to a minimum the possibility of surface denaturation.

The solution to be dialyzed may be introduced and removed with great ease and very little loss. Samples may be removed for analysis at any time during the dialysis.

The apparatus may be made from glassware available in any laboratory, and at slight expense.

The details of construction and the dimensions of the dialyzer are shown in Figure 2.

The fluid to be dialyzed is introduced through the opening of reservoir A. It then passes by means of a rubber connection down to the 5-mm. opening, B, from which it flows between the cellophane membrane, C, and tube D, which is closed off at both ends and fits snugly inside the cellophane tube. The solution is thus exposed for dialysis in a thin cylindrical layer, about 1 mm. thick. This fluid can then flow into tube F through the small (5-mm.) hole, E, and is kept circulating by means of nitrogen or other gas admitted by tube H. Bulb G permits the gas to collect under the fluid in the upper arm of F until the pressure is sufficient to force this fluid over in one slug. This has proved better than continuous bubbling when protein-containing solutions are dialyzed, since it checks foaming and minimizes surface denaturation. The solution being dialyzed may be removed through the side tube, J, which is closed by rubber tubing and a pinchcock.

The outer jacket, K, of the dialyzer is sealed at both ends by rubber stoppers, L. Either tap water or distilled water is admitted to this jacket through the side arm, M, from a reservoir which is set at a height sufficient to give a rapid flow of fluid without creating enough pressure to collapse the dialysis membrane. The outflow from the jacket occurs through tube N, which is of larger bore than the inflow tube.

Numerous dialyses with solution containing 900 mg. per cent protein precipitated by one-quarter saturated ammonium sulfate have been found practically salt-free within 6 hours.

To test the rate of loss of salt from the dialyzer, 100 cc. of a 50 per cent saturated solution of ammonium sulfate were put in and at various times 0.5-cc. samples were removed by the side tube, J. The samples were analyzed for their ammonia nitrogen by the manometric micro-Kjeldahl method of Van Slyke (5). The results, plotted in Figure 1, show that 98 per cent of this salt was removed in 9 hours. The rate of outflow from the outer jacket was 75 cc. per minute during the first 3 hours and was cut to one third during the last portion of the dialysis.

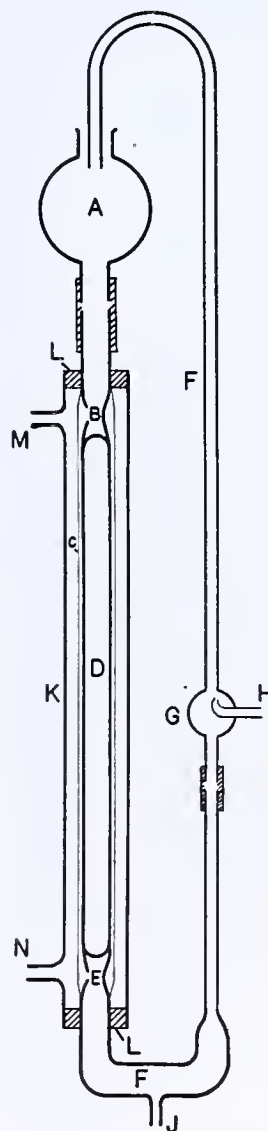


FIGURE 2. DIALYSIS APPARATUS

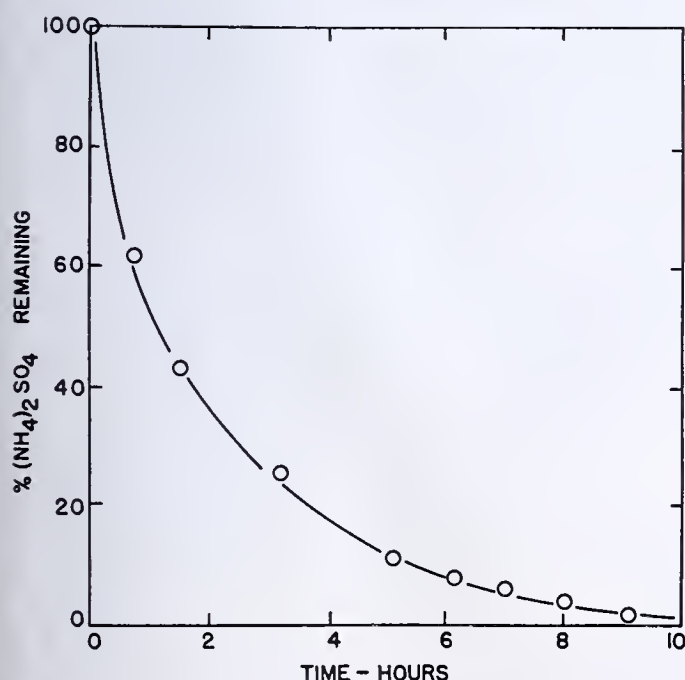


FIGURE 1. DIALYSIS OF 50 PER CENT SATURATED AMMONIUM SULFATE

Per cent of ammonium sulfate remaining in dialyzer at various times after start of experiment

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# MICROCHEMISTRY



## Accuracy and Precision of Microanalytical Determination of Carbon and Hydrogen

### A Statistical Study

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A direct empirical test of the accuracy and precision of the microanalytical determination of carbon and hydrogen, embracing 349 individual analyses of about 200 pure compounds by 23 experienced analysts, yields the information that this process is conducted at present with an over-all precision of about 2.9 parts per 1000 of carbon and about 22 parts per 1000 of hydrogen; both elements are determined slightly too high, the error on the carbon being probably significant and that on the hydrogen probably not.

The statistical methods used are described and illustrated briefly.

While tolerance limits expressed in per cent on the sample are not in accord with the usual custom among American chemists, such expression is sound in principle for carbon and hydrogen determinations. The outside tolerances for hydrogen as found from the present study agree very well with those commonly accepted; those on carbon, however, are a little wider than commonly accepted values.

The precision attained by microanalysts varies considerably and should be given due consideration by organic chemists.

Microanalysis is an art as well as a science.

THE accuracy of the microanalytical determination of carbon and hydrogen is a matter of considerable importance in organic chemistry, but unfortunately it seems also to be rather controversial. Niederl (28) sums up what the various authorities have to say on the matter—that is, for compounds not too abnormal in composition, the results of an experienced analyst should ordinarily come within  $\pm 0.2$  per cent of the theoretical carbon and hydrogen content of the substance, and should not exceed the limits  $\pm 0.3$  per cent. Since these limits are given by the authors on the basis of general experience, without presentation of specific and concrete data, it should be not only very interesting but also of value to chemists if these limits of accuracy were made more objective and definite by subjecting them to a direct empirical test, with the data analyzed afterwards by modern statistical methods.

Such a direct empirical test may be conducted in two ways: We may study the results obtained from the analysis of one pure compound by many chemists, or from the analyses of many pure compounds by one chemist. Both methods have been used in the present study.

### Accuracy and Precision

In none of the summaries on this general question is adequate distinction drawn between these two terms. Accuracy is here used as the conformity between the obtained result and the "true result". Precision is taken to mean the consistency of the obtained results among themselves. The distinction is in a broad sense that which exists between the objective and the subjective element in a set of physical measurements, although precision as usually expressed may possess a certain objective value. Indeed, after the exclusion of all known sources of error it becomes our chief criterion of accuracy. If accuracy be taken to mean the agreement between a given microanalysis and the theoretical percentage of carbon or hydrogen in a pure substance of known composition, the definition is sufficient for the purpose of this paper. It will be unnecessary, therefore, to go into the epistemological implications involved in the concepts of accuracy and precision, although many pages are devoted to this subject by statistical writers.

For a study of precision alone it would be sufficient to perform calculations on any controlled series of analyses of any homogeneous substance; but if the substances are pure and of known composition, a study of their analyses compared with theory will serve to calculate the accuracy as well as the precision of the analytical process.

### Methods of Approach

At the start of this study I had intended to rely primarily on the method of "one sample by many chemists", as has been done by the National Bureau of Standards on standard samples, by the Committee on Uniformity in Technical Analysis on samples of various ores (5), and by Lundell (25).

Samples of Bureau of Standards benzoic acid (standard sample 39e) were sent to several microanalysts both here and abroad, who were asked to report results on duplicate determinations of carbon and hydrogen. It seemed desirable also to try a compound of more complex composition, so a sample of Merck's ephedrine hydrochloride (serial 52,763), which had been used



satisfactorily as a test substance in our laboratory, was also sent. It melted at 218.3° (corrected), a value slightly higher than that given in the literature. The instructions called for giving these substances a preliminary drying at about 50° in the Pregl micro-desiccator. Reports on 18 samples were received (13 from the United States and 5 from Europe), to which are added the results of my assistant, Joseph Alicino, and my own.

The other method ("many samples by one chemist", Method I) was extended to "many samples by five chemists", as follows:

Four experienced microanalysts were asked to pick out at random from their laboratory notebooks 30 or more routine analyses on compounds of whose identity and purity there could be no question. Donald Price had carried out most of the microanalyses connected with the work of the late Dr. Hooker (23) and of Adelson and Bogert (1, 2), and the results under his name were taken from these articles. Adelbert Elek of Rockefeller Institute and Wm. Sáschek of the College of Physicians and Surgeons, Columbia University, wrote out lists of such analyses after consulting with the chemists who submitted the compounds for analysis, to make sure that they were reporting on substances of high purity. Alicino did the same and I have added a few of my own.

Methods of Calculation

All the errors dealt with in this paper were originally calculated in parts per 1000 of carbon and hydrogen, because (1) many different substances of varying carbon-hydrogen content are concerned; (2) at the outset the relation between precision and content was not known; and (3) this is the more common practice among American chemists. However, the practice in most microanalytical literature—i. e., expressing the error in per cent on the sample—has considerable justification.

The original data from the five laboratory notebooks (Method I) would be prohibitively lengthy if published in easily usable form; hence only a summary is presented. The original data of Method II (many chemists on one sample) are given in full.

The deviation of each individual analysis from theory was calculated in parts per 1000 of carbon or hydrogen, the difference being taken as positive where the analysis was higher than theory and as negative when it was lower. The algebraic sum of these deviations, divided by the number of analyses, gave the mean error of any particular series—that is, the accuracy of the analyses on the assumption that all the compounds were pure known substances. The differences between this mean error and the individual results were written down together with their squares. If we designate these differences from the mean error, without regard to sign, by *d*, and the number of analyses in the series by *N*, we may compute the so-called average deviation, *a*, and the standard deviation, *s*, by the usual formulas

a = Σd/N  
s = √Σd²/N

In the ideal case, as *N* approaches ∞, *s* approaches a limit designated as σ. Symbolically,

σ = Lim s  
N → ∞

An estimate of σ may conveniently be written σ<sub>s</sub>, to show that it is estimated from a sample. The most common estimate is

σ<sub>s</sub> = s√N/(N - 1) = √Σd²/(N - 1)

which for practical purposes, especially when *N* is large, may be written

σ<sub>s</sub> = √Σd²/N

The calculation of the average deviation, *a*, has been included in what follows, because it is probably more familiar to chemists and it seems to afford a fairly close estimate of the standard deviation from the analytical results in this paper. The standard deviation, *s*, is a convenient measure of dis-

person about the arithmetic mean of a distribution of errors, and the average deviation, *a*, is a convenient measure of dispersion about the median, a quantity practically never used by chemists. In the normal error curve, the mean and median coincide, and the theoretical relation between the average deviation and the standard deviation in an infinity of normal observations is the expression

σ = √1/2π a = 1.253a

Not knowing how closely these analytical results would approximate a normal distribution, I preferred to calculate the standard deviation by its own formula rather than by the use of the average deviation. The approximation to normality turns out to be close enough, with a corresponding agreement between means and medians. One of the specifications given by Bond (4) for a median type of distribution is that the precision of the individual determinations should vary in a haphazard manner, whereas the corresponding specification for a normal distribution is that the precision should be about the same for all the determinations. In the work described here, done by experienced analysts using very nearly the same detailed technique, the condition for a normal distribution would be expected. The use of the expression

σ<sub>s</sub> = 1.253a

as an estimate of the standard deviation is usually frowned on by statistical writers, however, since it is not only less efficient from a mathematical standpoint, but its indiscriminate use necessarily involves the assumption of a normal distribution in cases where this may obtain only very approximately.

The analyses in the five laboratory notebooks (Method I) were all calculated on the basis of C = 12.00, using the corresponding gravimetric factor 0.2727. If the more recent value of C = 12.01 (3) and its gravimetric factor 0.2729 had been used, the final figure for the precision would suffer no change, but a slight effect would be noted on the average agreement between analysis and theory. Rather than ask the analysts to recompute their results on the basis of C = 12.01, it is considered sufficient to correct the average error of each analyst's list by adding 0.5 part per 1000. This is arrived at by computing the per cent of carbon calculated and found on a compound of about the average composition of all these substances—i. e., about 63.9 per cent carbon—and comparing the results using C = 12.00 with those for C = 12.01. If the analytical error on such a compound is found to be, for instance, 4.0 parts per 1000 high on the basis of C = 12.00, the error will be 4.5 parts per 1000 high on the basis of C = 12.01. Table I, a summary of all these analyses, has been corrected in this way.

TABLE I. METHOD I					
(Summary of results, one chemist on many samples)					
Analyst	Number of Individual Analyses	Mean Error	Median Error	Standard Deviation	Standard Deviation
				Calculated directly: $\sigma_s = \sqrt{\Sigma d^2 / N}$	Calculated from a: $\sigma_s = 1.253a$
Parts per 1000					
Carbon (C = 12.01)					
Elek	58	+0.4	+0.4	1.2	1.2
Power	37	+1.2	+1.8	4.2	4.3
Price	48	-0.3	-0.1	2.4	2.4
Alicino	77	+1.3	+1.1	2.8	2.7
Saschek	61	+1.1	+0.8	2.3	2.1
Hydrogen (H = 1.008)					
Elek	58	+3	+1	9	8
Power	37	-5	-3	20	20
Price	48	+10	+15	25	27
Alicino	77	+8	+5	21	20
Saschek	61	-6	-5	18	19
CONDENSED FORM OF ABOVE DATA					
				C	H
Number of individual analyses				281	281
Standard deviation, parts per 1000				2.5	18
Mean error of analysis, parts per 1000				+0.8	+2.6



Any analyst by using the statistical methods employed here can calculate the accuracy and precision of his own results on the same assumptions as are made here—namely, that the compounds are pure substances of known composition, that he chooses the analyses without prejudice, and that enough is taken to give a reasonable approximation to the statistical laws for large samples. About 150 individual analyses would be a minimum for this purpose.

### Comparison of the Methods

When a preliminary report was presented (31), the results by these two methods of approach agreed fairly well, but as more data accumulated it was clear that the accuracy and precision estimated by the cooperative analysis on the two test samples were going to be considerably lower than those obtained from the five laboratory notebooks.

Method II is probably the more objective, being dependent only on the purity of the test substances and not open to choice or interpretation by me or by the cooperating analysts. Against it is the fact that it does not correspond to the ordinary routine procedure in organic research, where the composition of a substance is usually judged on its repeated analysis by the same person; hardly ever does a research director send an unknown compound to many different analysts. Furthermore, the use of such a method, involving only two rather simple substances, would not give a true cross section of a procedure which in practice involves all sorts of substances of widely differing composition.

Method I is open to the serious objection that it is less objective—that is, anyone would naturally be inclined to select analyses on the basis of their close agreement with theory rather than on the basis of sample purity. In collecting these 281 individual analyses, however, this danger was reduced to a minimum, and while they probably do not satisfy all the requirements for a truly random sampling in a statistical sense, they approach it nearly enough for practical purposes.

I propose, therefore, to use the results obtained from these analyses as a criterion to be applied to the results obtained by Method II. Some individual analyses on this list were so far away from theory that a fair estimate of accuracy would necessitate applying some criterion of rejection, which would look like begging the question. It would seem, however, that such a procedure can be justified. It was not proposed to make a crude estimate of the accuracy of a process whose error had never been investigated before, but rather to attempt a methodical refinement of a quantity which has been known by many years of practical experience. Only a few of the cooperating analysts had any idea what use was to be made of their reports; it did not suit the purpose to have them run the analyses with any special precautions. Results obtained in the regular course of the day's work were wanted. Under these conditions it is to be expected that an occasional analysis will go wrong; and the few results that are highly discrepant, and which will subsequently be rejected, illustrate that when a man says he can "check a result to 0.3 per cent" he should add "in so many analyses out of a hundred".

### Criteria of Significance and Rejection

Of the indefinitely large number of possible frequency curves, the normal curve, usually associated with the name of Gauss, is most commonly used as a basis for the statistical study of physical measurements. For this purpose it is usually written

$$y = \frac{N}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

where  $y$  is the frequency of occurrence of an error of magnitude  $x$  away from the arithmetic mean of  $N$  measurements, which

are controlled by standard deviation  $\sigma$ . In statistical work, however, it is customary to plot the frequency as a function of  $t$  rather than of  $x$ , where  $t = x/\sigma$ , thus expressing the error as some fraction or multiple of the standard deviation. In a strictly normal distribution of an indefinitely large number of measurements, the expression

$$P = \frac{N}{\sigma\sqrt{2\pi}} \int_0^t e^{-\frac{t^2}{2}} dt$$

gives the probability of occurrence of a chance, random, or indeterminate error between zero and  $t$ . Since in analytical work we expect errors of both signs, it is usually more convenient to take twice this integral, giving that fraction of the measurements affected by random errors over the range  $-t$  to  $+t$ .

While the normal curve is widely used as a basis for statistical treatment of physical measurements, its limitations for this purpose must be taken into account, and the treatment of its various advantages and disadvantages is gone into *per longum et latum* by the statistical writers. For practical purposes of error theory the normal curve is only a mathematical convenience, the use of which is based largely on pragmatic grounds. Its most obvious limitation lies in the fact that it can be approximated only when very large numbers of measurements are available, which may not always be the case in chemical work. Then, too, the very large random errors which the normal curve would require cannot occur when an experienced investigator performs repeated high-precision measurements by recognized techniques on the same invariable object; this is the chief basis for the statement that the normal curve is only a fairly close approximation to the distribution of measurements made in a very poorly conducted experiment. This very point, however, is made the basis of a simple and very commonly used criterion of rejection.

If we consider a measurement giving a very large value of  $t$ , we see that it has a very low probability of having occurred by chance, and for practical purposes this statement may be reversed to read that highly discrepant measurements have a high probability of not belonging to the series of concordant measurements affected only by random errors—that is to say, measurements of high  $t$  values may be rejected as being affected by errors which are real or significant. Just what  $t$  value to select as a criterion of rejection is a matter of opinion; the larger we take it the more lenient we shall be in admitting widely discrepant values among the measurements accepted as valid.

Fisher (12) and many other statistical writers regard those deviations as significant which exceed twice the standard deviation. In the limiting case of a normal distribution of a very large number of measurements, this would mean that we enter the probability table (19) at  $t = 2$  and find the corresponding probability to be 0.955, which under the assumptions mentioned may be taken to mean that 955 measurements out of 1000 may be expected to show chance deviations (from the mean) whose magnitude will not exceed twice the standard deviation. Conversely, the other 45 measurements, whose deviations from the mean exceed twice the standard deviation, may be said to be affected by errors which are not due to chance but are determinate or significant errors. Some authorities set this "critical ratio" higher than  $t = 2$ ; for example, Ostwald and Luther (29) take  $t = 2.5$ , while Shewhart (42) uses  $t = 3$ , not so much on account of the particular value of the probability associated with it (0.9973) but because "experience indicates that  $t = 3$  seems to be an acceptable economic value". In certain statistical applications to experimental psychology and education even higher values are used.

For most analytical work one will be safe in taking the value  $t = 2$ —that is, if an individual measurement differs from the mean of the series by an amount greater than twice the standard deviation of the individual measurements in the series, one will usually be justified in suspecting it as a valid member of the series. Or if a given analysis, conducted with the usual care necessary to exclude all known errors, gives a result differing from the expected value by more than twice



the standard deviation of the analytical process, one will usually be safe in suspecting either the identity or purity of the compound. If these are shown to be unexceptionable, the chances are that a determinate error has crept in despite the vigilance of the analyst.

Observations or measurements which may be treated statistically may be grouped in two classes, according to their material objects. In one class would be, for example, the stature of men, the size of maple leaves, the blowing time of fuses, the weight of newborn infants, the rainfall in New York, the market price of a group of commodities, etc. In the other class would be most physico-chemical measurements, such as the atomic weight of an element, the velocity of light under a given set of conditions, the equatorial diameter of the earth, etc.

For the purposes of this paper it is necessary and sufficient to note one important distinction between these two classes of measurements. In the first class the mean value which the investigator is looking for has itself no physical existence in nature prior to the calculations; the investigator makes it. In the second class the mean value actually exists in nature prior to the calculations; the investigator is trying to find it. The variations encountered among individual observations or measurements of the first class are due primarily to the diversity of the individuals themselves and secondarily or not at all to the imperfections and limitations of the measuring process. In the second class the variations encountered are not due to the object being measured, since it is a definite extra-mental entity, but arise entirely from the imperfections and limitations of the measuring process itself.

It is advisable to emphasize these points because statisticians usually object strenuously to rejecting any observation; and rightly so, if it belongs to the first class described. For example, if one is getting the average height of men one cannot reject an individual in the agreed-on population merely because his height is  $3\sigma$  below that of the group. He might be rejected as a prospective police officer, but he cannot be rejected as a man.

On the other hand, certain of our better physico-chemical techniques are per se incapable of such wide variations, and if such should be observed, the experienced investigator who has checked and rechecked this technique may logically ascribe unusually wide discrepancies to the sample rather than to the method of measurement. In other words, he may justly have such confidence in the method as to conclude that he is taking measurements coming under the first classification rather than the second. The classical instance of this is the discovery of the rare gases through high-precision measurements of the density of nitrogen from different sources.

While the ordinary daily procedures of microanalysis do not fall under this category, they do possess a certain precision which when once established and applied can serve as a basis for judging highly discrepant results as being due either to the impurity or identity of the sample or to some inadvertence on the part of the analyst in controlling the known sources of error.

The present article will serve as a general estimate of the precision of these processes, representing a cross section for many analysts; but no chemist will be justified in using these numerical data to establish a criterion of rejection for his own work unless he has found by actual test that his accuracy and precision are the same or very nearly the same as those set down here as a sort of over-all estimate. Furthermore, the use of any such criterion in a given analysis will be governed less by statistical considerations than by a critical evaluation of the analysis from a purely microchemical viewpoint—the personal assurance that all the necessary precautions have been taken to exclude all known and determinate errors in a given analysis.

An interesting statistical test analogous to the use of  $t$  as a criterion of rejection would be to apply this calculation to the mean values from Table I. Just as the standard deviation of the individual determinations measures their scatter or dispersion around their arithmetical mean, so the standard deviation of the mean value itself (called the standard error of the mean) is a measure of the dispersion of various mean values of  $N_1, N_2$ , etc., individual determinations around the "grand mean" of a very large number of determinations, the standard error of the mean of  $N$  observations being

$$\sigma_M = \frac{\sigma}{\sqrt{N}}$$

The corresponding  $t$  value will be

$$t = \frac{\Delta x}{\sigma_M}$$

where the magnitude of  $t$  will indicate in a general way whether any given discrepancy— $\Delta x$ , for example—between a given analytical mean and the theoretical value, may be reasonably ascribed to accidental errors or whether it should be considered to indicate a constant error of analytical significance.

From Table I we have estimates of  $\sigma_M$  as follows, with  $N = 281$ :

$$\sigma_M = \frac{2.5}{16.76} = 0.15 \text{ part per 1000 for carbon}$$

$$\sigma_M = \frac{18}{16.76} = 1.07 \text{ parts per 1000 for hydrogen}$$

and the values of  $t$  for the mean discrepancies from theory will be

$$t = \frac{0.8}{0.15} = 5.3 \text{ for carbon}$$

$$t = \frac{2.6}{1.07} = 2.4 \text{ for hydrogen}$$

The reader should distinguish carefully between the magnitude of an error and its significance. In this case, the pooled results of Table I indicate that both the carbon and hydrogen analyses were affected by a small positive error; but the  $t$  value would incline one to conclude that this error would not ordinarily have arisen by chance or indeterminate errors, but that rather it represents a real, although perhaps trivial, error inherent in the analytical process.

### Method of "Many Chemists on One Sample"

In Table II are given the original unselected analyses reported on the two test substances. The analysts are designated by letters according to the order in which their reports were received. The carbon results, both calculated and found, are on the basis of  $C = 12.01$ .

A summary of Table II is given in Table III, as it may be considered the most objective set of data presented in this paper.

DISCUSSION OF TABLE II. These results are rather disconcerting. Testing them against their own means and standard deviations they are not bad; theoretically only four or five carbons and hydrogens should exceed twice the standard deviation, and actually only five carbons and one hydrogen are outside this range. The chemist, however, is interested in testing the analyses against the theoretical values, and using a more reasonable estimate for the standard deviations of the process. If we assume these to be 2.9 parts per 1000 for carbon and 22 parts per 1000 for hydrogen (the final values arrived at in this paper), we find 18 carbons and 16 hydrogens differing from theory by more than twice these standard deviations. Since this is really testing a series of measurements against a mean and a standard deviation not derived from the series itself, these figures cannot be given a strictly statistical interpretation, but the practical analyst's interpretation would probably not be very complimentary. Furthermore, one may count 31 carbons and 18 hydrogens which fail to meet Pregl's outside tolerance of  $\pm 0.3$  per cent



TABLE II. ORIGINAL UNSELECTED ANALYSES (METHOD II)

Analyst	Benzoic Acid		Ephedrine Hydrochloride		Analyst	Benzoic Acid		Ephedrine Hydrochloride	
	C	H	C	H		C	H	C	H
	%	%	%	%		%	%	%	%
A	69.03	5.00	59.22	8.19	J	69.14	5.32	59.84	7.51
	68.96	4.91	59.66	8.31		69.24	5.27	59.84	7.55
B	69.18	5.22	59.23 <sup>a</sup>	7.76 <sup>a</sup>	K	69.06	5.05	59.65 <sup>d</sup>	7.82 <sup>d</sup>
	69.22	5.19	59.27	7.86		68.99	5.01		
C	69.58 <sup>b</sup>	5.54 <sup>b</sup>	59.60	7.56	L	69.01	5.56 <sup>b</sup>	59.49	7.97
	69.43	5.38 <sup>b</sup>	59.46	7.72		69.23	5.51 <sup>b</sup>	59.55	8.17
D	68.79	5.01	59.55	8.07	M	68.55	5.40 <sup>b</sup>	60.44 <sup>b</sup>	7.86
	68.98	5.10	59.23	8.08		68.70	5.13 <sup>d</sup>	60.19 <sup>b</sup>	7.84
E <sup>c</sup>	69.23 <sup>a</sup>	5.06 <sup>a</sup>	59.54 <sup>a</sup>	8.12 <sup>a</sup>	N	68.99	5.05	60.42 <sup>b</sup>	8.01
	69.17 <sup>a</sup>	4.81 <sup>a</sup>	59.68	8.02		69.10	5.09	60.21 <sup>b</sup>	8.10
	69.17	4.81	59.63	7.94	O	68.72	5.02	59.45	8.07
	68.85	4.88				68.81	4.99	59.63	7.94
F	68.67 <sup>a</sup>	5.10 <sup>a</sup>			P	68.94	4.99	59.54	7.99
	69.14	5.03	59.87	7.80		68.86	4.93	59.56	8.01
G	69.42	5.06	59.86	7.66	Q	68.92	5.19	59.91 <sup>a</sup>	7.86 <sup>a</sup>
	68.86	4.92	59.43	7.95		69.46	5.15	59.12	8.27
H	68.73	4.96	59.59	8.02	R	68.92	4.93	59.46	8.06
	68.86	5.04	59.09	7.79		68.85	4.96	59.70	7.59
I	68.81 <sup>a</sup>	5.02 <sup>a</sup>	59.17 <sup>a</sup>	7.85 <sup>a</sup>	S	68.93	5.04	59.86	7.68
	68.84	5.03	59.27 <sup>a</sup>	7.72 <sup>a</sup>		68.92	4.96	59.79	8.00
			59.13 <sup>a</sup>	7.64 <sup>a</sup>	FWP <sup>e</sup>	68.92	4.96	59.65	7.98
			59.10	7.88		69.24 <sup>a</sup>	4.92 <sup>a</sup>	59.51	8.24
			59.14 <sup>a</sup>	7.65 <sup>a</sup>		68.88	4.89	59.75 <sup>a</sup>	8.16 <sup>a</sup>
			59.77 <sup>a</sup>	7.64 <sup>a</sup>		69.04	4.76	60.24 <sup>b</sup>	8.26
	68.80	5.03	59.81	7.71				59.61 <sup>a</sup>	8.04 <sup>a</sup>
	68.83 <sup>a</sup>	4.87 <sup>a</sup>						60.27 <sup>b</sup>	8.07
	68.95	4.96	59.72	7.66				59.60	8.00

<sup>a</sup> Excluded at random from Table III.  
<sup>b</sup> Excluded as too inaccurate for Table III.  
<sup>c</sup> Analyst, J. Alicino.  
<sup>d</sup> Excluded from Table III for want of a duplicate.  
<sup>e</sup> Analyst, F. W. Power.

TABLE III. SUMMARY OF RESULTS OF TABLE II

	Benzoic Acid		Ephedrine Hydrochloride	
	C	H	C	H
Theoretical per cent	68.84	4.952	59.55	7.995
Mean per cent from analyses	69.00	5.140	59.62	7.930
Median per cent of analyses	68.96	5.03	59.60	7.94
Actual error of mean (from theory), parts per 1000	+2.3	+38	+1.2	-8
a, %	0.18	0.17	0.26	0.17
s, %	0.22	0.20	0.34	0.21
s, parts per 1000	3.2	40	5.7	26
s, parts per 1000, calculated from a	3.3	43	5.4	27

(from theory), or about 25 per cent of all the individual analyses.

The accuracy of the mean analytical results is much better on the ephedrine, a compound presumably inferior in purity to the Bureau of Standards benzoic acid; the precision on the latter is better than on the former for carbon, but much worse for hydrogen.

RECONSTRUCTION OF TABLE II. It is only fair to take into account certain extenuating circumstances in connection with some of these analyses. One of the two men who reported very high results did the analyses on one of the hottest and most humid days of the summer of 1937, as was the case with one of my own analyses. The other used a technique which may occasionally admit undried air to the absorption tubes. Another analyst, whose results are rather badly out of line, used a gas velocity different from that usually recommended, as he was working on a problem which required such a modification and did not reset his pressure regulators. In this case, too, there was some question as to contamination of one of the samples. There are two sets of high carbons reported by European analysts and one high carbon of my own for which no apparent explanation can be given.

From a purely statistical standpoint one would hesitate to reject any of these analyses, but from a chemical standpoint some question can be raised as to the purely random character of some of the larger errors. There should be no serious objection, therefore, to reconstructing Table II. In the first place I propose to apply to all the data of this table a very lenient criterion of rejection—namely, the theoretical percentages plus or minus four times the standard deviations

already deduced from the results of Table I. These results have certain points in their favor; and besides, such a wide tolerance will exclude only those few analyses which have evidently been affected by some determinate errors. The theoretical percentages are selected as the basis of the criterion of rejection so as to give information as to the accuracy of the process; but in the reconstructed table the standard deviations will naturally be calculated from the actual means of the analyses. From the analyses meeting this tolerance I propose to select at random two results in those cases where more than two were reported, so as not to overweight the results of any one analyst.

The reconstructed table will consist of 17 duplicate analyses within the following tolerance ranges:

	C	H
Benzoic acid	68.15 to 69.53	4.60 to 5.32
Ephedrine hydrochloride	58.95 to 60.15	7.43 to 8.57

The new table is not given *in extenso*, but can be made by writing down those analyses in Table II not noted in footnotes as having been excluded. If a hydrogen analysis failed to meet the above tolerances, the corresponding carbon value was not used, and vice versa. Table IV gives a summary, made up in the same way as was Table III.

Since in all but one instance each chemist reported more than one analysis, the final standard deviation, representing the total variance of all the analyses, is really a composite quantity; part of the variance is due to discrepancies among the results of any one analyst and part to discrepancies among

TABLE IV. SUMMARY OF RECONSTRUCTED TABLE II

	Benzoic Acid		Ephedrine Hydrochloride	
	C	H	C	H
Theoretical per cent	68.84	4.952	59.55	7.995
Mean per cent from analyses	68.99	5.022	59.55	7.916
Median per cent of analyses	68.95	5.02	59.59	7.96
Actual error of mean (from theory), parts per 1000	+2.2	+14	Zero	-10
a, %	0.14	0.088	0.18	0.174
s, %	0.18	0.119	0.23	0.212
s, parts per 1000	2.6	24	3.8	26
s, parts per 1000 calculated from a	2.5	22	3.8	27



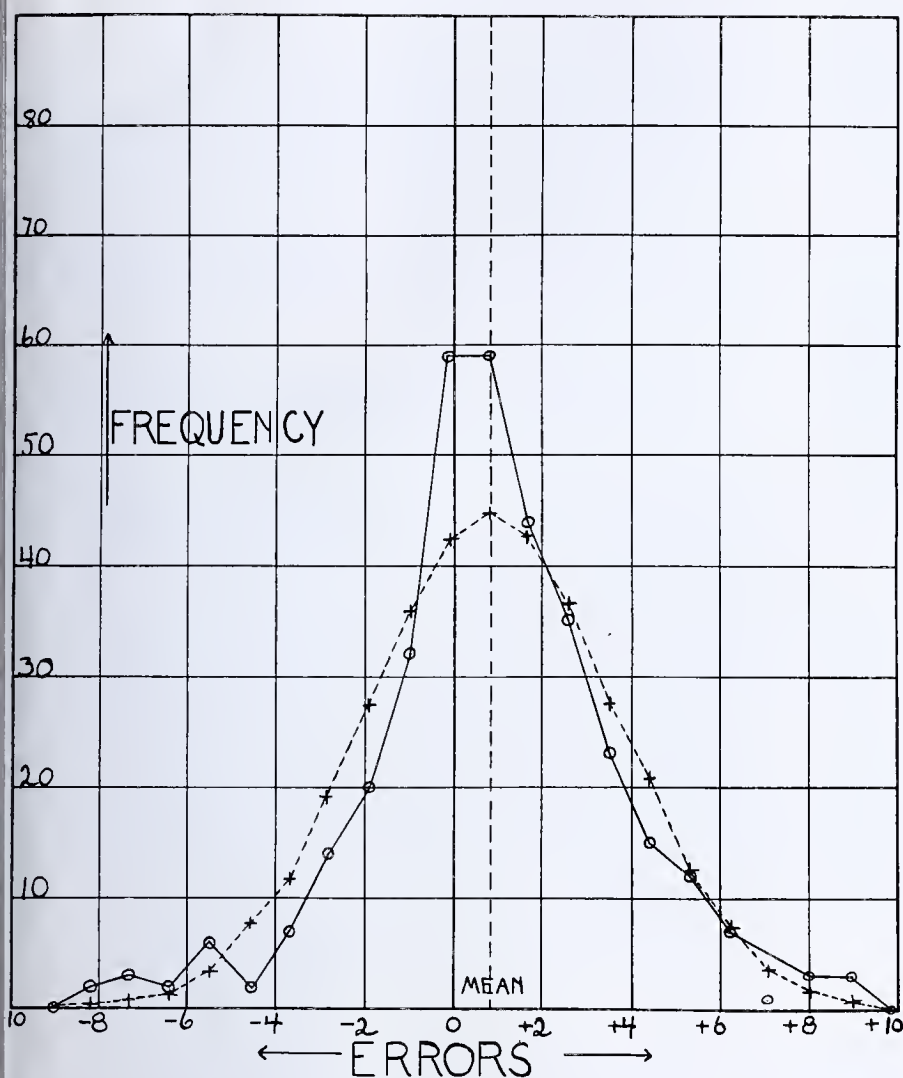


FIGURE 1. FREQUENCY CURVE FOR CARBON ANALYSES

The analytical errors on carbon, in parts per 1000, are plotted as abscissas and the frequency of their occurrence is plotted as ordinate. The total number is 349. The smooth curve in dashed line is that of the normal curve for  $N = 349$ ,  $\sigma = 2.9$ .

he chemists themselves. Statistical methods (known as the analysis of variance) are available (18, 37, 46) whereby one may assign a certain degree of statistical probability to the influence of these two factors. On performing this operation on Table II (before it was quite complete), the various chemists checked their own results much better than their colleagues' results—that is, the variations in the results of the different analysts were much larger than could be accounted for solely by the variations within the work of each one. A similar variance analysis on reconstructed Table II showed that for the hydrogen determination on benzoic acid and for both carbon and hydrogen on the ephedrine, the agreement within the duplicate analyses done by any one man was significantly better than that between the different analysts. The reverse was true of the benzoic acid carbon.

The mathematical analog of these carbon and hydrogen analyses in Snedecor's book (46) is the yield of bacon from different breeds of hogs! It is a good illustration of wide application of modern statistical methods.

**SUMMARY OF ANALYTICAL DATA.** Giving equal weights to the results from Tables I and IV we may make the following general summary:

Method	Standard Deviation		Mean Error (Actual Deviation from Theoretical)	
	C	H	C	H
	Parts per 1000		Parts per 1000	
One chemist on many samples	2.5	18	+0.8	+2.6
Many chemists on one sample	3.2	25	+1.1	+2.0
Av.	2.9	22	+0.9	+2.3

A test for significance on these final figures gives:

	C	H
$N$	349	349
$\Delta x$	0.9	2.3
$\sigma_M$ (estimated)	0.153	1.20
$t$	5.9	1.9

showing a high probability that the slight over-all positive error on the carbon determination is significant, but that the considerably larger positive error on the hydrogen is accidental.

Another test on the entire collection of analyses would be to see how closely they approximate a normal distribution. One standard method for doing this is to compute the skewness and the flatness of the entire collection, involving the third and fourth moments, respectively, of the distribution. The information thus gained, however, while of considerable academic interest, would hardly compensate for the added amount of computation, which increases considerably when one goes beyond the squares of the deviates. The skewness for some of the individual lists in Table I was found near enough to zero to warrant using the normal curve for the distribution rather than a Gram-Charlier series or any of the many other frequency distributions noted in books on statistical analysis.

In order more easily to visualize the statistical distribution, all the analytical data from Table I and reconstructed Table II have been plotted as frequency curves, the results for carbon in Figure 1 and those for hydrogen in Figure 2. Here the analytical errors in parts per 1000 are plotted as abscissas and the frequency of their occurrence as ordinates. Along with the actual frequencies are shown those required for the corresponding theoretical normal

curves. In these cases each analysis is given equal weight, while in the summary above the pooled results of Table IV were weighted equally with those from Table I. The carbon results in both are corrected to the basis of  $C = 12.01$ .

A visual comparison of the observed frequencies with those calculated is rather deceptive. The curves are leptokurtic—i. e., too sharply peaked. Once a mean value has been estimated, the form of any frequency curve is set for all practical purposes by three parameters—the standard deviation, the coefficient of skewness, and the coefficient of flatness—functions controlled, respectively, by the second, third, and fourth powers of the deviates. These curves are not noticeably skewed, but the departure from normality appears most marked in the center, in that the measurements are better than normal—that is, there are more analyses of high precision than a strictly normal distribution would require. There is, however, a mathematical criterion for the "goodness of fit" of a set of observed values to a hypothetical or calculated set of values; this is the so-called "chi-square test" of Karl Pearson, whereby one calculates

$$\text{Chi-square} = \sum \left[ \frac{(\text{frequency calculated} - \text{frequency found})^2}{\text{frequency calculated}} \right]$$

This test is described in many books (13, 17, 36). The values of chi-square are tabled as a function of the number of pairs of values or groups of values summed up, and one may see from these tables the frequency by which any chi-square is exceeded by chance. In general, for a given number of classes



summed, the larger chi-square, the worse the fit. This test on the foregoing data yields the following results (kindly checked by Joseph Kubis of the Department of Psychology):

	Carbon	Hydrogen
Number of analyses	349	349
Number of classes summed	15	13
Chi-square	31.9	20.8
Probability	<1%	8.6%

These low probabilities do not indicate a very close correspondence with the normal curve; the fit for the hydrogen would do, but that on the carbon is definitely poor although not impossible. Perhaps contrary to ordinary expectations, the parts of the curve for carbon contributing most to the large chi-square value are not the center nor the tails, but the negative errors between 1 and 5 parts per 1000. However, the discrepant frequencies causing the poor fit of the curve are those cases where the precision of the analyses was better than the normal curve would require.

**DISCUSSION.** In conducting such an investigation as this, where the analysis is judged by the compound rather than the compound by the analysis, the purity of the test substances is obviously of prime importance. With regard to the cooperative analysis on the benzoic acid and ephedrine, any misgivings about the purity of ephedrine are somewhat allayed by the fact that it "analyzed closer" than did the Bureau of Standards benzoic acid. The many compounds taken from the records of the four analysts were carefully selected by competent analysts, who knew exactly what was required and who spent considerable time interviewing the chemists

who prepared the substances, to be assured that they were dealing with known compounds which had been specially purified for purposes of research and publication.

Any statistical treatment of physical measurements can be concerned only with that complexus of errors which we usually call indeterminate—that is, those which are left over and unaccounted for after all known and controllable sources of error have been eliminated. In the results here recorded there is, however, one determinate error included with the others—namely, the buoyant effect of the air on the sample and on the absorption tubes.

The buoyancy effect on the weighing of samples would be negligible as a rule, since the density of most organic compounds is near enough to the density of the aluminum rider against which they are weighed to keep the error from this source below 1 part per 1000. The buoyancy effect on the absorption tubes, however, is another matter. Presumably all the analysts used the usual system recommended by Pregl (33) of counterpoising them against small glass bottles loaded with lead shot, and in this case the change in buoyance with changes in atmospheric conditions may be appreciable, as was noted by Schwarz-Bergkampff (38) and Williams (49). The latter gave figures on the variations due to change in air density on the glass weighing bottles used in some of his experiments, and calculated that when these were counterpoised with the usual shot bottles they should undergo an apparent change in weight of about 6 micrograms per degree of temperature and about 23 micrograms per centimeter of atmospheric pressure. My own calculations for the actual tubes and tares used in the carbon and hydrogen analysis agree substantially with his (32). The volumes of solids in the Anhydron and Ascarite tubes are about 2.8 and 4.0 cc., respectively, while the volumes of the corresponding tare bottles with the necessary lead shot are about 1.3 and 1.4 cc.; from these figures one may calculate an apparent change in weight of about 7 micrograms per degree of temperature and about 23 micrograms per centimeter barometer on the water tube and 11 and 40 micrograms, respectively, on the carbon dioxide tube.

The ordinary changes in humidity during the course of the day will have no appreciable effect as far as buoyancy is concerned; however, the other two atmospheric variables have a very appreciable effect on a given analysis, especially on that for carbon, and Williams' point is well taken namely, that the tares should be made almost entirely of glass so as to minimize this temperature effect. At all events, it is certain that no microanalyst takes the necessary data to make the corrections, and that no one has given this error its due consideration; so it must of necessity be put into the category of statistical errors. This error, however, will hardly affect the final result significantly, and in the course of the 349 analyses that comprise the present data, this differential effect of buoyancy may reasonably be expected to include about as many positive as negative errors and cancel out nearly enough for the present purpose, although in any one analysis or group of analyses run the same day this could by no means be assumed.

The absolute value of the buoyancy correction for the products of combustion need not be taken into account for purposes of microanalysis. The greatest ordinary correction necessary in this connection is in the case of weighing water against brass weights, where it amounts to about 1 part per 1000. Here, however, we are dealing with weights—i. e., the counterpoises—whose density does not exceed 6.5 (and should be kept around 2.5); the density of the substance being weighed is presumably that of anhydrous magnesium perchlorate ( $d = 2.6$ ), an equivalent amount of which goes to either the trihydrate ( $d = \text{about } 2.3$ ) or the hexahydrate ( $d = 2.0$ ) as the combustion proceeds. Such small differences in density between object and weight put the error from this source considerably outside the precision that these methods are ordinarily capable of giving, although for the purpose of atomic weight determinations by combustion of hydrocarbons (3) these factors must be taken into account.

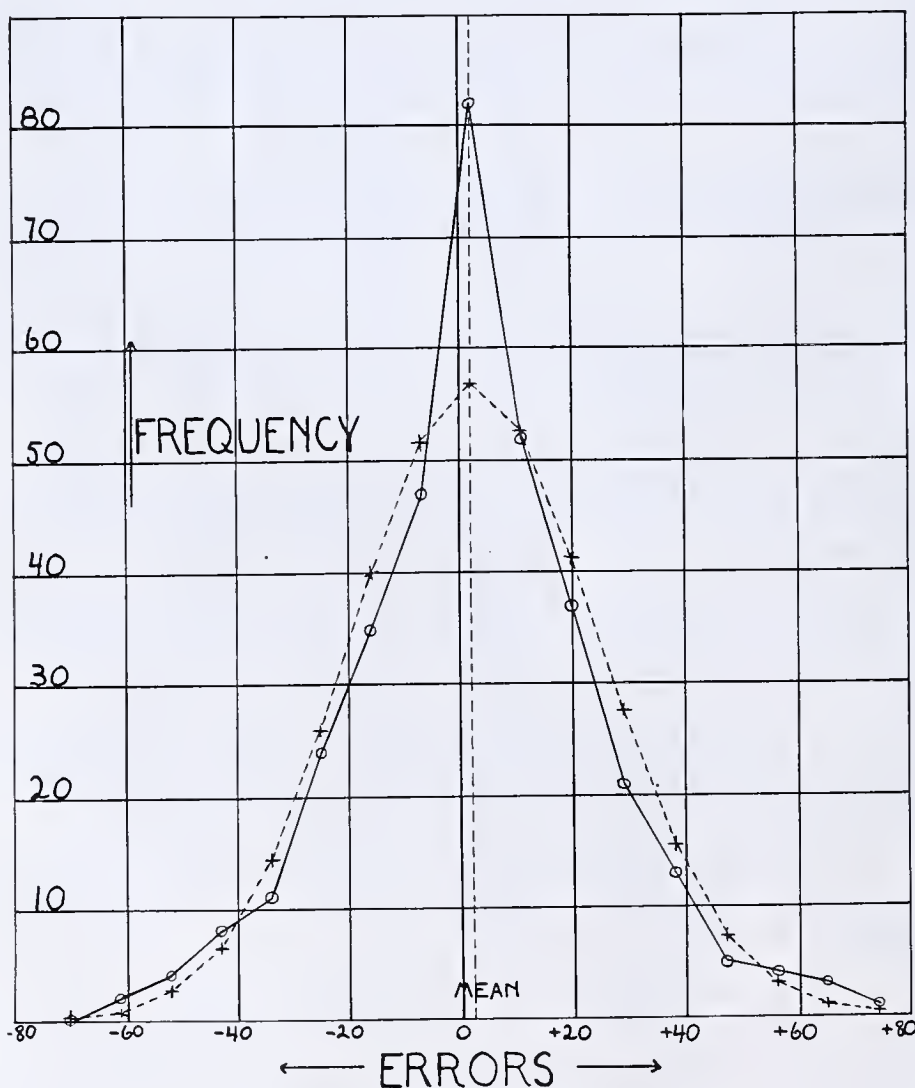


FIGURE 2. FREQUENCY CURVE FOR HYDROGEN ANALYSES

The analytical errors on hydrogen, in parts per 1000, are plotted as abscissas and the frequency of their occurrence is plotted as ordinate. The total number is 349. The smooth curve in dashed line is that of the normal curve for  $N = 349$ ,  $\sigma = 22$ .



As to the precision of these micromethods, compared with the older methods using about 100 times as much sample, although I know of no explicit published analysis on macro-methods similar to the one made here, a statement in Fisher's book (10) lends itself to a good comparison. In the section on macrocombustions Fisher states that the "allowed" error should not exceed 2.5 parts per 1000 for carbon and 20 parts per 1000 for hydrogen. Presumably he is referring here to compounds of fairly normal composition, and his allowed error I take to be identical with the average deviation of the individual analyses from theory.

For approximate purposes it will be sufficient to calculate from this the standard deviation from the relation  $\sigma = 1.253a$ , whence we obtain 3.1 and 25 parts per 1000 for carbon and hydrogen, respectively, for the macroprocess as compared with 2.9 and 22 parts per 1000, respectively, which are my final results for the microprocess. One would hardly expect such striking agreement. The obvious conclusion is that while some microanalysts can and do obtain a precision twice as good as this, the over-all precision and accuracy of micro-combustions taken by and large are not significantly superior to those attained by the older methods, although in economy of time and material there is no comparison.

Ingram (24), in describing a modified Pregl semimicro setup, gives several analyses on pure substances which offer an interesting comparison along this same line. There are 26 individual analyses in his list, run on 14 compounds. His data work out as follows:

	Carbon	Hydrogen
	Parts per 1000	
Mean discrepancy from theory	-0.7	+17
Standard deviation	2.4	17
Standard error of mean	0.47	3.3
$t = \frac{\Delta x}{\sigma_M}$	1.49	5.16

These figures show a probably nonsignificant error on carbon about the same as that deduced here; the error on hydrogen, however, which is significant, is a little better than the one I give. The precision is about the same.

Absolute and Relative Criteria of Accuracy

The absolute criterion given by Pregl and most other authors has so far not been employed—i. e., that the analysis should ordinarily check the theoretical composition of a pure known substance within  $\pm 0.2$  per cent and that the error should not exceed  $\pm 0.3$  per cent. With the foregoing figures, however, together with others given below, we are in a position to justify such a criterion in principle, and even to come close to it numerically.

It is elementary that precision and accuracy are in approximately inverse ratio to the amount of the constituent being determined in the sample; also that the accuracy of the determination of a given constituent is best referred to its content in the sample, not to the whole sample itself. However, if the approximation to the inverse ratio be established by actual experimental results, the use of an absolute criterion is allowable. Such approximation to an inverse relation between precision and content can be tested by substituting the estimated values in the expression

(% C x sigma\_C) / (% H x sigma\_H)

which should equal unity for a strictly inverse relation. The assumption is made here that the lower relative precision on the hydrogen is due not to any inherent analytical difficulty peculiar to hydrogen, since in the one apparatus both carbon and hydrogen are determined simultaneously by the same process, but rather to the magnification of the various errors

(common to both constituents) due to the correspondingly lower content of hydrogen in the ordinary run of organic compounds.

This relation of precision to content may now be worked out from two sets of combustions—namely, those of Baxter and Hale (3) and those reported in this paper.

In the recent revision of the atomic weight of carbon by means of the precision combustion of pure hydrocarbons, Baxter and Hale weighed both the water and the carbon dioxide in a series of most carefully conducted experiments, and from these we can obtain an exact picture of the precision as an inverse function of the content. On the basis of their results on triphenylbenzene, anthracene, and chrysene, one may calculate the following general averages:

Carbon content, %	94.37
Hydrogen content, %	5.624
s (carbon), part per 1000	0.084
s (hydrogen), part per 1000	0.800
Ratio: % C / % H = 16.8	
Ratio: s_H / s_C = 10.5	

For a strictly inverse relation between precision and content we should have

(% C x sigma\_C) / (% H x sigma\_H) = 1.00

instead of which (using s as an estimate of sigma) it comes out 1.76. The same figures for the microanalyses herein described, the carbon and hydrogen contents being the mean of 200 substances taken at random from the original data of Table I, combined

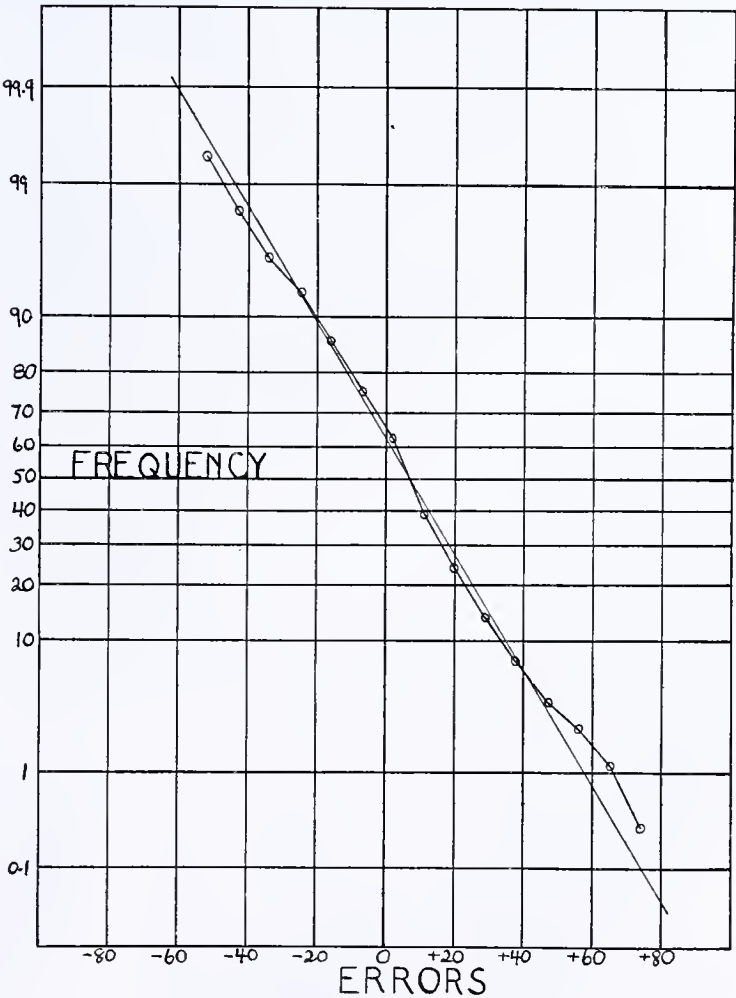


FIGURE 3. FREQUENCY CURVE FOR HYDROGEN ANALYSES

Same as Figure 2, but plotted on probability paper, ruled to rectify normal curve (22). This plots as a straight line, while the actual distribution plots as a wavy line. Departure from the slope of the normal line indicates skewness; but the leptokurtic quality of the curve in Figure 2 hardly appears on this graph. Here the abscissas are the analytical errors in parts per 1000, but the ordinates are the cumulative frequencies, expressed as per cent of the total number of analyses (349).



on equal terms with the percentages in the two test substances, are:

Carbon content, %	63.87
Hydrogen content, %	6.67
$s$ (carbon), parts per 1000	2.9
$s$ (hydrogen), parts per 1000	22
Ratio: $\frac{\% C}{\% H} = 9.6$	
Ratio: $\frac{s_H}{s_C} = 7.5$	

This relation, which should equal unity, is here 1.27.

The data of these two series represent almost the antipodes of precision, those of Baxter and Hale exceeding ours by 34 to 1 on carbon, and by 27 to 1 on hydrogen. Despite this great discrepancy, however, they agree in this, that the precision obtained on the two constituents is very close to the inverse of the amount of constituent present. It also follows that the relative precisions given in this paper are really those of an average organic compound containing about 64 per cent of carbon and 6.7 per cent of hydrogen; for compounds of higher content the standard deviations expressed in parts per 1000 will be correspondingly lower, and vice versa. I would not care to say, however, what precision one could attain on such compounds as iodoform where the amount of hydrogen is extremely low.

While the relative precision (expressed in parts per 1000 of carbon or hydrogen) varies inversely with the amount of carbon and hydrogen in the compound, the absolute precision (expressed as per cent of carbon or hydrogen, on the whole sample) should remain about the same for the range of all ordinary compounds. Expressing the standard deviations obtained from the micro results already given in absolute percentages on the sample of average composition, we have:

$$\frac{63.87 \times 2.9}{1000} = 0.18\%$$

$$\frac{6.67 \times 22}{1000} = 0.14\%$$

These figures, converted into the average deviation (which is what the books mean by the ordinary agreement with theory) equal about 0.15 per cent for carbon and 0.12 per cent for hydrogen, as compared with the usual criterion of 0.2 per cent. Some of the more recent authors, cited by Niederl, are a little stricter than Pregl in this criterion of ordinary agreement. The outer limits of acceptance set arbitrarily at twice the standard deviation come out approximately 0.36 per cent for carbon and 0.29 per cent for hydrogen. Therefore while Pregl's ordinary criterion is rather lenient, his outside limit is about right, although it can be stretched a little in the case of the carbon determination.

The definition of accuracy at the beginning of this article would afford very little consolation to those who determine atomic weights, but the above comparative figures will explain why the definition is all right for those who perform ordinary microanalyses.

**HOW MANY ANALYSES?** One very interesting application of the statistical method relates to the number of analyses necessary for some given degree of statistical probability that the result will agree with theory within some given amount. There are serious difficulties involved in making this application, but it is well worth mentioning. A statement of precision in physical measurements always carries with it the implication that the precision mentioned can be attained in a definite proportion of the measurements made. The complete relation is stated by Shewhart (43): "Assuming that we know that a quality  $X$  is normally controlled with standard deviation  $\sigma$ , how many measurements of this quality must we make in order that the probability will be, let us say, 0.9973 that the deviation of the average of  $N$  observed values from the true

but unknown arithmetic mean be not greater in absolute magnitude than some given value  $\Delta x$ ? From what has previously been said we see that the size,  $N$ , of the sample required in this case is rigorously given by the relation  $\Delta x = 3\sigma/\sqrt{N}$ ."

The figure 3 is the value for  $t = x/\sigma$  corresponding to the probability 0.9973 which Shewhart uses as his criterion of significance for the sort of statistical control work with which his book is largely concerned and the value of which is here taken as  $t = 2$  for analytical work. Putting the foregoing statement into terms of analytical chemistry, we may say that it will be necessary to perform  $N$  determinations on a substance to have the statistical odds 21 to 1 ( $t = 2$ ,  $P = 0.955$ ) that the average of these  $N$  determinations will come within  $\Delta x$  parts per 1000 of the theoretical value, provided these  $N$  analyses were all performed with precision  $\sigma$ .

An example will illustrate the use of this relation in the ideal case where the standard deviation of the individual analyses is known and no constant error is present. Suppose a choice has to be made between two empirical formulas for a certain compound; according to one formula it should contain 60.00 per cent of carbon and according to the other it should contain 60.20 per cent, and the chemist would be satisfied if he could be certain of the analysis—i. e., with the odds 21 to 1 in its favor, or  $t = 2$ —within  $\pm 0.05$  per cent.  $\Delta x$  then becomes 0.10 per cent or 1.7 parts per 1000, and it is assumed that the process is conducted with a precision represented by  $\sigma = 2.9$  parts per 1000 on carbon.

These quantities are then substituted in the above equation and we have

$$\sqrt{N} = \frac{2 \times 2.9}{1.7} = 3.41$$

whence we see that 11 or 12 individual analyses will be necessary and sufficient to decide on the formula under the foregoing assumptions.

There are two difficulties which in practice make such a simple application difficult: One is the presence of a possibly significant constant error in the analytical process, and the other is the difficulty of estimating the standard deviation and assuming it to apply to any particular small series of combustions. If a constant significant error is present nothing can be done about it; even though the analyst may have established the magnitude of such an error over a long series of determinations, he is hardly justified in assuming that it has the same value in a short series. Then, too, the assumption that an over-all standard deviation which represents the indeterminate errors over a long series represents them equally well here is not well founded. However, for general directive purposes and in the long run this application can be made, provided the chemist is aware of its limitations. This formula, which is really the theoretical relation between accuracy and precision, has been used in other connections; Munch (26) employs it (in the form of the probable error) to calculate how many animals are required in bioassays, and Haynes and Judd (20) make use of it in this same form in connection with studies in the properties of certain fruit juices. It is used implicitly by Scott (39), who gives a very interesting and detailed statistical study of the blood sugar of rabbits.

**SMALL-SAMPLE TECHNIQUE.** The British scientist W. S. Gossett, writing under the pseudonym of "Student" (the name by which he is always referred to in the statistical literature), published in *Biometrika* in 1908 a now famous article (15) in which as his first problem he proposed a method for locating the value of the "true mean" when only a few observations were available.

Using the normal curve of probability and on the basis of our 349 measurements, we could state that the analyses in the long run are high by

$$0.9 \pm \frac{0.6745 \times 2.9}{\sqrt{349}} = 0.9 \pm 0.10 \text{ part per 1000}$$

for carbon, and



$$2.3 \pm \frac{0.6745 \times 22}{\sqrt{349}} = 2.3 \pm 0.79 \text{ part per 1000}$$

for hydrogen, using the expression for the probable error of the mean. That is to say, according to the "classical" error theory, there is 50 per cent probability that the mean error on carbon for a very large number of analyses will lie in the range +0.8 to +1.0 part per 1000, and 50 per cent probability that it will lie outside this range.

Suppose, however, that only four analyses were available—could the normal curve of probability still be used as a basis for estimating where the true mean lies? "Student's" answer is no; in its place he proposes a family of skew frequency curves which approach the normal curve as a limit as the size of the sample increases. His curve for  $N = 30$  is sensibly identical with the normal curve.

Taking "Student's" function for  $n = 4$  and interpolating for  $P = 50$  per cent, or using Table II in Deming and Birge's article (7), we find that the "Student" 50 per cent limits for a mean of 4 will be  $0.442s$ , where

$$s = \sqrt{\frac{\Sigma d^2}{4}}$$

According to the normal law the probable error of a mean of 4 would be

$$\frac{0.6745 \sigma}{\sqrt{4}} = 0.337 \sigma$$

where  $\sigma$  would be estimated (for such a small sample) from the formula

$$\sigma_s = \sqrt{\frac{\Sigma d^2}{3}}$$

To take a concrete sample, if the errors of four analyses for carbon gave a mean of +0.35 part per 1000, with  $\Sigma d^2 = 87.740$ , the usual estimate of the probable error of the mean would be

$$0.6745 \times \sqrt{\frac{87.74}{3}} \times \frac{1}{\sqrt{4}} = 1.82 \text{ parts per 1000}$$

According to "Student's" curve for  $n = 4$  it would be

$$0.442 \times \sqrt{\frac{87.74}{4}} = 2.06 \text{ parts per 1000}$$

The range within which the mean of the "universe" would be expected (to a probability of 50 per cent) would be therefore (as most authors give it)  $-1.47$  to  $+2.17$  parts per 1000 by the usual theory, and  $-1.71$  to  $+2.41$  parts per 1000 by "Student's" function.

On this interpretation, the estimated probable error range, in the case of small samples, locates the mean in a narrower range than "Student's" method. The difference is more marked when we wish to increase our assurance and hence extend the range within which the mean of the universe may be expected. Thus if we propose to set a range within which the mean may be expected to a probability of 95.5 per cent, we find that this corresponds to a range of  $\pm 2\sigma_M$  using the normal curve, which in the example just given would be a range estimated to be  $-5.07$  to  $+5.77$  parts per 1000. Using "Student's" system, however, we interpolate in his tables (using  $2P - 1$  instead of  $P$  so as to cover both sides of the curve) and find the coefficient  $z$  (as he calls it) to be 1.94; hence the range will be (mean  $\pm zs$ ) =  $+0.35 \pm (1.94 \times \sqrt{\frac{87.74}{4}})$  or  $-8.75$  to  $+9.45$  parts per 1000.

One does not get much consolation out of a range as wide as this, but when only four observations are available one cannot expect very much, nor can this range be expected to check another one taken later on a different group of four analyses.

In order to emphasize the danger in statistical estimates made from small numbers of observations, I submit a random sampling experiment summarized on what Shewhart calls a "control chart"; frequent examples of these are found in his book, and one of the charts is given also by Deming and Birge (7, p. 141). Their chart, however, is based on an artificial

"universe", whereas the one presented here is constructed from some of the analyses used in this present paper.

From each one of the five laboratory notebooks mentioned (Method I) 36 analyses for carbon were selected at random, and expressed as errors (from theoretical carbon) in parts per 1000, thus giving a universe of 180 actual analyses done by five different men. The analyses were numbered serially and identical round brass checks were procured, numbered consecutively from 1 to 180, put into a large evaporating dish, and thoroughly mixed. An assistant then withdrew at random four of the checks, and the four corresponding analyses were written down. These four checks were replaced in the dish and the contents mixed thoroughly, after which four more checks were withdrawn at random and the corresponding analyses written down. This process was repeated 100 times.

The mean and standard deviations ( $s = \frac{1}{2}\sqrt{\Sigma d^2}$ ) of each of these 100 samples of four were then calculated; also the mean and standard deviations of the whole 180 taken as one group. The 50 per cent ranges for means of 4, according to "Student's" function, were then written as (mean of 4)  $\pm 0.442s$ . The 100 means were then marked on a graph (Figure 4) in the order in which they were drawn and the 50 per cent ranges corresponding to each one were laid off vertically above and below the spot marking the mean. Finally, horizontal control lines were drawn, the center one at the mean of the whole 180 analyses, and upper and lower lines at distances of plus or minus the probable error of a mean of 4 calculated from the standard deviation of the universe. The values of these various quantities were found to be

	Part per 1000
Mean of 180 analyses	+0.36
Standard deviation of individual analyses, calculated from all 180	$\frac{2.69}{\sqrt{4}} = \pm 0.91$
Probable error of a mean of 4	

This control chart will serve to test the effectiveness of "Student's" method in setting the range within which the mean of the universe may be expected to a probability of 50 per cent. According to this, the mean of the universe should be found in one half the cases to lie within the sample ranges, and the other half of these ranges should fail to include or overlap the mean of the universe.

By actual count from Figure 4 we find cases of the mean of universe as follows:

	Within Sample Ranges	Outside Sample Ranges
Calculated	50	50
Found	44	56

Of the actual mean values themselves 52 are inside the control lines and 48 outside. This is not a serious discrepancy, and may be due to the departure of my figures from a strictly normal distribution, which is what "Student" explicitly assumes as a basis for his functions.

If, however, we now expect to be able to estimate the precision of the measuring process by an extension of this method, we shall find a serious difficulty on again inspecting Figure 4. "Student" (15) assumes, and even goes to some pains to prove, that there is no correlation between the mean of a sample and its standard deviation. On this point the chemist would say that it is possible to get, for example, four analyses whose mean is almost exactly that calculated for the compound and yet which are very badly discrepant; in fact, the chemist will find in his own work examples of all four combinations: high accuracy, high precision; high accuracy, low precision; low accuracy, high precision; low accuracy, low precision.

If we look on the 100 results in Figure 4 as 100 pages of an analyst's notebook we shall find there these same examples—on pages 19, 83, 53, and 87, respectively. For purposes of test, the lower the precision of a group of measurements the easier it is to locate the true mean from that particular group, since the range is larger. However, if the chemist proposed to estimate the precision of his process solely on the four analyses on page 7 of his 100-page notebook (Figure 4), what a flattering picture this would be! And how disappointed he would be when he proposed to check this result later, using the analyses on page 83 whose average is "right on the dot" but whose precision is only  $\frac{1}{26}$  as



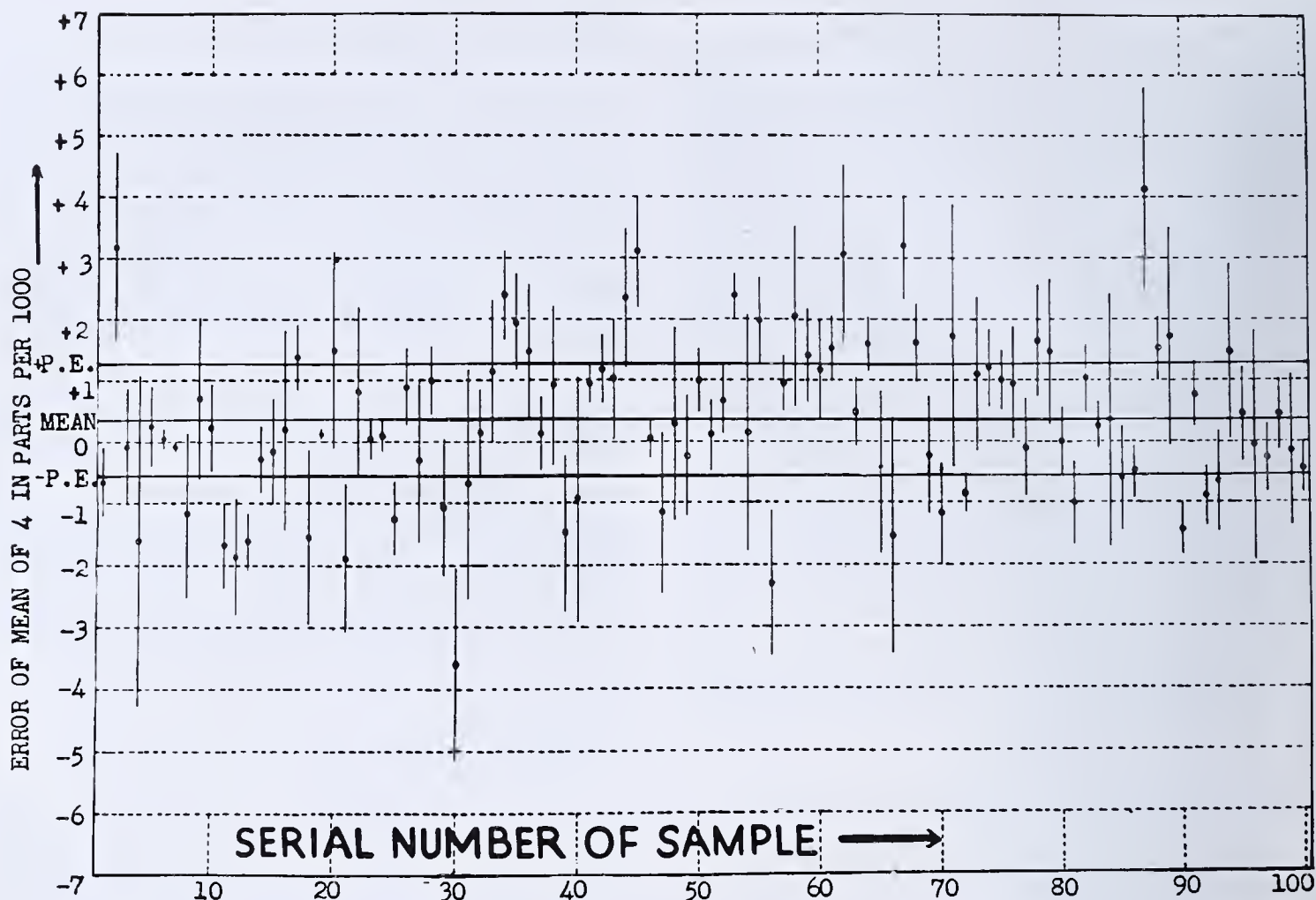


FIGURE 4. CONTROL CHART FOR SAMPLES OF 4 (CARBON) (44)

The ordinates represent the analytical errors in parts per 1000 of the means of 4 carbon analyses drawn at random with replacement from a universe of 180 analyses from Method I. These means are set down from left to right in the order in which they were drawn. Above and below each point representing the mean of each sample of 4 is drawn a vertical line representing the "Student" 50 per cent limits for that sample. The upper and lower horizontal lines indicate the probable error of a mean of 4 estimated from the universe ( $= \pm 0.90$  part per 1000). The central horizontal line marked mean is placed at the mean of the universe ( $= +0.36$  part per 1000).

good. Since the number of analyses necessary for a given degree of accuracy goes up as the square of the standard deviation, our chemist's second estimate would require him to run over 600 times as many analyses as would his first estimate! Here the case is set at its worst, using samples of only four and picking two extreme cases from the control chart; but it will serve as a horrible example of what happens when one subjects even the most scientific-looking arithmetic to the vagaries of the sampling errors of small numbers of measurements.

As another illustration of this point, using much larger samples, the same universe of 180 analyses from which Figure 4 was constructed was divided into three groups of 60 analyses each by withdrawing at random without replacement 180 brass checks, each corresponding to one analysis. The following were the results:

	Mean	Standard Deviation
	<i>Parts per 1000</i>	
1st series of 60	-0.15	2.85
2nd series of 60	+0.75	2.97
3rd series of 60	+0.47	2.17
Universe of 180	+0.36	2.69

Here the means seem affected as badly as the standard deviations. If some trusting person, content with what he found in most of the books, after doing the necessary calculations on the first 60 analyses stated that "95.5 per cent of all future means will lie within the range  $\pm 2\sigma_M$ ", or within

$$\pm 2 \times \frac{2.85}{\sqrt{60}} = \pm 0.74 \text{ part per 1000}$$

of the mean -0.15 part per 1000, he would do so in blissful ignorance that the mean of the very next series would lie 0.16 part per 1000 outside this range. Or, if he ventured to predict the values of future standard deviations by the rule that the standard

deviation of the standard deviation is  $\frac{\sigma}{\sqrt{2N}} = \frac{2.85}{\sqrt{120}} = 0.26$  part per 1000 and stated that "95.5 per cent of all future standard deviations on series as large as this will lie within the range  $2.85 \pm 0.52$  part per 1000", he would be unaware that the next series but one turns up a standard deviation 0.16 part per 1000 outside this range.

Small-sample technique (or micro statistics, if I may strain a point) is all right for the purpose for which it is intended; but for predictive purposes and for setting tolerance ranges the chemist will find it of little practical use, since for any sort of statistical assurance the ranges necessarily become so wide as to have little practical meaning. This point is emphasized by Deming and Birge (7). Besides, the chemist's measurements seldom constitute a really normal, random, statistical universe; as Shewhart puts it, they are not "controlled" (44). This whole matter is treated in a masterly fashion by Scott (39). If worse comes to worst, and small samples have to be used to estimate the standard deviation of the universe, about all that one can do is to use the median, modal, or mean estimate from the standard deviation of the sample (8, 30, 41), which for samples of 4 would be  $\sigma = 1.300s$ ,  $\sigma = 1.415s$ , and  $\sigma = 1.253s$ , respectively. A test from Figure 4 for median  $\sigma$  gives a fair agreement with theory. The authors agree, however, that these procedures are at most an attempt to make the best of a bad job.

FISHER'S TESTS FOR SIGNIFICANCE. "Student's" functions are most commonly used in statistical work nowadays in the



form suggested by Fisher (11) and for the purpose of testing whether the mean of a unique sample differs significantly from zero, and whether two means differ significantly from one another, the standard deviations being estimated from the samples themselves, which are assumed to be small. This application is explained and the tables are given not only by Fisher but in many other texts on statistical methods (14, 16, 35).

Out of the many examples of these applications to analytical work two are selected, one for each of the cases just mentioned.

Wieland (47), in investigating the structure of a certain natural pigment, had to make a choice between a single- and a double-molecule formula for his compound, relying largely on the carbon-hydrogen microanalysis for his choice. The data are:

	Carbon	Hydrogen
Calcd. for $C_{10}H_{10}O_6N_8$ , %	35.49	2.98
Calcd. for $C_{19}H_{19}O_{11}N_{18}$ , %	36.00	3.02
Found (mean of 7), %	35.80	2.78

It is obviously impossible to make any distinction using the hydrogen figures, but some information may be gained from the carbon. Taking the deviation of each individual analysis from 35.49 per cent (on the hypothesis of a single-molecule formula) we find a mean difference of +0.31 per cent. Taking the squared differences of each of the above deviations from +0.31 we get a sum of 0.2089. To use Fisher's own nomenclature (14) we have:

$$\begin{aligned}\bar{x} &= +0.31 \quad n' = 7 \\ s^2 &= \frac{S(x - \bar{x})^2}{n' - 1} = \frac{0.2089}{6} = 0.0348 \\ t &= \frac{\bar{x} \sqrt{n'}}{s} = \frac{2.646 \times 0.31}{0.1865} = 4.40\end{aligned}$$

The same process is repeated, taking differences from 36.00 per cent of carbon on the hypothesis of a double-molecule formula, with the results:  $\bar{x} = -0.20$ ,  $s^2 = 0.0348$  (the same as before), and  $t = 2.84$ .

These  $t$  values are then looked up in Fisher's  $t$ -table for  $n = 6$ , one less than the number in the sample. The largest value of  $t$  on  $n = 6$ , corresponding to  $P = 0.01$ , is 3.707, which is far smaller than the  $t$  value just obtained for the single-molecule formula. (Fisher does not carry his table below the 1 per cent point.) This is taken to mean that there is less than 1 chance in 100 that the difference between the carbon found and carbon calculated is due merely to chance errors—that is, it is highly probable that a real difference exists between the analytical figure and 35.59 per cent. It is extremely unlikely, therefore, that the single-molecule formula is correct. The other value,  $t = 2.48$ , looked up on  $n = 6$  corresponds to  $P = 0.033$ , indicating 3.3 per cent probability that chance errors could account for the difference between carbon found and carbon calculated on the basis of the double-molecule formula.

Offhand one would naturally select the latter, since it agrees closest with the analysis, but it is interesting to see how the statistical method leads one to the same conclusion, although without a great deal of cogency, since the  $t$  test here really shows that there is very little absolute probability in favor of either formula. About all we can say is that relatively one is far more improbable than the other. Wieland presents other arguments in favor of his choice of the double-molecule formula (48).

As an example of testing for the significance between two mean values the following might be apposite. Two chemists performed microanalyses on the same sample of pure benzoic acid; the mean of Mr. A.'s 7 carbons was 68.81 per cent while Mr. B. ran 5 determinations with a mean of 68.96 per cent. Is this difference to be ascribed merely to the indeterminate errors of the analytical process, or does it represent a real and significant difference between the techniques of the two operators? Using again Fisher's nomenclature we have:

$$\begin{aligned}\bar{x} &= 68.81 \quad \bar{x}' = 68.96 \quad n_1 = 7 - 1 = 6 \quad n_2 = 5 - 1 = 4 \\ S(x - \bar{x})^2 &= 0.0894 \\ S(x' - \bar{x}')^2 &= 0.1950 \\ s^2 &= \frac{0.0894 + 0.1950}{6 + 4} = 0.0284 \\ s &= 0.1686 \\ t &= \frac{\bar{x} - \bar{x}'}{s} \sqrt{\frac{(n_1 + 1)(n_2 + 1)}{n_1 + n_2 + 2}} = \frac{0.15 \times 1.705}{0.1686} = 1.516\end{aligned}$$

This  $t$  value is looked up on  $n = n_1 + n_2 = 10$  and here we find  $P = 0.23$ —that is, there is 23 per cent probability that the difference between the two analysts is due to chance, and since this is fairly large we conclude that no significant difference exists between the techniques of the two operators. In practice, unless  $P \leq 0.05$  (corresponding to  $t \geq 2.23$ , on  $n = 10$ ) we would not ordinarily consider the difference significant.

These significance tests are widely used by statisticians, and chemists need not feel restricted to the rather outmoded methods found in most of their reference and textbooks (6). Used, however, as illustrated above, they labor under the difficulty of relying on a standard deviation estimated from a rather small number of observations. In tests such as this, the authors distinguish two kinds of errors that may occur: The rejection by the test of a given hypothesis which is objectively true is called an error of the first kind; the acceptance, on the basis of the test, of a given hypothesis which is objectively false is called an error of the second kind (27).

In this connection, "Student's" methods (whether used in the form he gave them or in that proposed by Fisher) are particularly designed to test the hypothesis that a given sample mean is equal to the mean of the universe—that is, to test the significance of the difference between these two means. "Student's" system would be as follows:

$$\begin{aligned}x &= \text{sample mean} \\ \mu &= \text{mean of the universe} \\ s &= \sqrt{\frac{\sum d^2}{n}} \\ z &= \frac{\bar{x} - \mu}{s}\end{aligned}$$

$P(z, n)$  = probability that the value of the mean of the universe, in terms of the standard deviation of the sample, will lie between  $-\infty$  and  $z$

For analytical work it is better to take this as  $|2P - 1|$ , which will be the probability that the interval  $\pm zs$  will include the mean of the universe. Without prior knowledge of the value of the true mean, but on the hypothesis that it is zero, a value is assumed for  $z$ , corresponding to some desired probability, and the value of the quantity  $zs(\bar{x} - \mu)$  gives the difference between the sample mean and zero; the larger this is, the more "significant" the departure from the hypothesis. For a given assumed value of  $z$ , this difference or significance is set by the value of  $s$  for that particular sample.

Figure 4 was constructed in this way, assuming  $z = 0.442$ ,  $P = 50$  per cent. With prior knowledge of the value of the true mean—e. g., that it actually is zero—a test may be instituted (from Figure 4) to see in how many cases errors on the first and second kind actually have occurred. If we interpolate in "Student's" tables on  $n = 4$  for  $2P - 1 = 0.9500$  we find  $z = 1.84$ . According to his system, in 95 per cent of the cases the mean of the universe should lie within the range  $\bar{x} \pm zs$ ; for practical analytical purposes we may consider that the other 5 per cent of the cases ( $z > 1.84$ ) may be rejected, since here the mean of the universe should be outside this rather wide range.

In the table from which Figure 4 was calculated there are actually 4 values where  $z > 1.84$  instead of the 5 cases required by theory, an excellent agreement. In order to evaluate this as an empirical test, however, it is necessary to see that actual analytical errors are involved in the cases of these four means which the  $z$  test has rejected. Here again it will be necessary to assume some range for their rejection, independent of this test; for this is used twice the standard deviation for carbon already deduced as a final result in this present article, reduced here to that of a mean of four—i. e.,  $2 \times 2.9/\sqrt{4} = 2.9$  parts per 1000. Any sample means in Figure 4, therefore, differing from the mean of the universe by this amount, should be rejected independently of the  $z$  test, and those within this range should be retained. The mean of the universe of 180 (which is not so extensive as it might be) is known to be +0.4 part per 1000; hence the absolute range of acceptance will be  $-2.5$  to  $+3.3$  parts per 1000 of carbon. Of the four cases rejected by the  $z$  test none in my table is outside this range. Here, then, are four cases where results which would be acceptable in an absolute sense are rejected by the test—that is, four errors of the first kind.

Considering the errors of the second kind (again from Figure 4 where the mean of the universe is assumed to be known), we



inspect the actual errors of the 100 sample means and find 3 outside the above absolute range whose  $z$  values are less than 1.84—that is, there are three errors of the second kind. It would seem that one kind of error is just as bad from the standpoint of the organic chemist as the other, so here we have a total of 7 errors out of 100 possibilities of random sampling. This is not so bad with such small samples, but this very restricted experiment is not offered as a justification or criticism of the wide use of these significance tests by statistical writers.

If the original universe is far from normal and the samples drawn from it are small, the errors would undoubtedly be large—Shewhart (45) shows an example somewhat like this in his monograph. In such cases, particularly, one should be hesitant about drawing conclusions concerning structure until derivatives have been prepared and analyzed, as can almost always be done. I doubt whether the authors lay enough stress on the point that a normal universe is a prerequisite for "Student's" or Fisher's small-sample technique. What is more important is to be sure that a universe exists at all, normal or otherwise; none does until statistical control has been established.

### Advantages of Higher Precision

The point that one's time is better spent in improving precision than in running large numbers of rechecks is important enough to warrant one or two numerical examples.

When the old chemists were confronted with a choice between the alternative formulas for cholesterol

	C %	H %
$C_{26}H_{44}O$	83.80	11.90
$C_{27}H_{46}O$	83.87	11.99

they realized that combustion analysis on the substance itself would never get them very far, as can be seen from the following figures:

	Carbon	Hydrogen
Range (assumed), %	$\pm 0.014$	$\pm 0.018$
$t$ (assumed)	2	2
$\sigma$ (assumed)	2.9	22
Number of analyses required	305	215

This is clearly a hopeless task. This particular situation was first clarified 50 years ago by the combustion analyses of Reinitzer (34) on cholesterol acetyl dibromide; he checked the theoretical analysis of this derivative to 1.7 and 9 parts per 1000 of carbon and hydrogen, respectively. If this difficult choice on cholesterol itself had to be made on the basis of only one analysis, however, it could be made decisively by the technique of Baxter and Hale. Fieser and Jacobsen (9) went into this matter very thoroughly a few years ago and reported very interesting results, including a choice between two formulas differing by 0.34 per cent in carbon and 0.14 per cent in hydrogen on a sapogenin which had given widely discrepant results in the hands of several experienced analysts who used ordinary macro- and microprocedures. They settled the matter by two precision combustions, and one would really have been enough.

This sort of atomic weight technique cannot be recommended for ordinary research and control work, since even this precision does not often compensate for the fact that it involves running one combustion every other day on gram samples; but it is a striking exemplification of what a square root sign means in an equation.

### Bad Compound vs. Bad Analysis

A perennial controversy arises when the analyst's figures do not agree with the formula expected by the person who did the synthesis; the latter is as sure that the analyst did a poor job as the analyst is that the compound was "no good". Let us suppose that an analyst runs 500 combustions a year with an over-all precision of 2.9 and 22 parts per 1000 of carbon and hydrogen, respectively; this will allow him an absolute error of about 0.36 per cent on carbon and 0.30 per cent on hydro-

gen, taking average values for many compounds to cover the year's analyses. If the errors are normally distributed, 95.5 per cent should lie within this range of  $\pm 2\sigma$ , and 4.5 per cent should lie outside this range. According to the theorem of Tchebycheff (21, 40), which applies to this case as stated, the estimated error on these figures should not exceed  $t^{-2}$  or about 25 per cent. When confronted with badly discrepant figures by the individual who synthesized the compounds, our average analyst could admit that he was in the wrong about 23 times a year, or about once every two weeks; the rest of the time he could lay the blame on the impurity of the compounds. From practical experiences, however, I doubt if such statistical considerations would afford him sufficient protection!

### Recommendations

Those who depend largely on microanalytical data in their research work should first, know their analyst and be sure that he always acts on the scriptural injunction, "Prove all things—hold fast that which is good." Secondly, they should not take too seriously results obtained under very unfavorable weather conditions. Thirdly, they should see that the analyst runs test substances frequently, especially when a particularly critical point is being decided, and lastly, remember that his results follow in a general way the error function, whose curve has a certain finite spread; in other words, he is not expected to be right all the time.

### Acknowledgments

I wish to express sincere thanks to all who have cooperated with me on this problem, especially to the four chemists whose figures were used in Table I. I am also deeply indebted to Josef Solterer of Georgetown University and to W. A. Shewhart of the Bell Telephone Laboratories, Inc., for their valuable criticisms and suggestions along the lines of the statistical theory involved; and I owe a special debt of gratitude to Jack W. Dunlap of the University of Rochester for the help he has always generously given in studying and applying statistical methods to this and other problems undertaken in our laboratory. W. Edwards Deming of the U.S. Department of Agriculture has also rendered invaluable assistance, and I wish to thank him for putting his skill and experience at my disposal with such generosity and patience.

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# Volumetric Estimation of Lac on Glazed Candies

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THE widespread use of lac for coating candies and the establishment by the new Food, Drug, and Cosmetic Act of a maximum permissible lac content have stimulated interest in the development of a method for the estimation of semimicroquantities of the material. The method presented here, based on the extraction and the titration of the lac acids with standard sodium carbonate, is quick and simple enough to be used in control testing in the manufacture of glazed candies.

## Requirements of the Food, Drug, and Cosmetic Act

The production of arsenic- and lead-free lac enabled candy manufacturers to use lac coating on candies to serve a double purpose: (1) to form a protective seal, and (2) to produce a desirable glaze.

The Food, Drug, and Cosmetic Act (2) allows the use of such harmless glaze, but not in excess of 0.4 per cent. A manufacturer of candies, well before the law went into effect, asked the authors to render analysis on the lac content of his candies, in order to modify his manufacturing procedure if necessary and to ascertain that his products are within the law. A search of the literature showed no methods for the estimation of lac on glazed candy, but various articles (1, 3, 7, 8, 11) dealing with the chemical composition of shellac, none of which could be used for quantitative estimation in a complex system such as candy. The United States Department of Agriculture, Food and Drug Administration, advised (9) that they had had little or no occasion to determine glaze on candy quantitatively; hence they have no immediately available method for quantitative analysis of glazed

candy for shellac content. The need for a quick and accurate method is obvious. In manufacturing, a quick control with results obtainable within a few hours is essential, so that before the candies are packed the manufacturer may be certain that his product is within the requirements of the law.

## Discussion

In the manufacture of glazed candies the glaze is applied by means of a solution of pure lac in specially denatured alcohol 35, an authorized formula (10) for a solvent in manufacturing candy glazes under code 015. This formula is prepared by the addition of 35 gallons (9.25 liters) of ethyl acetate to 100 gallons (26.4 liters) of pure ethyl alcohol. Tests run on samples of refined lac such as is used in the candy industries showed that alcohols 35, 2B, and 3A were satisfactory solvents. Alcohol 2B is made by adding 0.5 gallon of benzene to 100 gallons of ethyl alcohol, and alcohol 3A by adding 5 gallons of commercially pure methyl alcohol to 100 gallons of ethyl alcohol. (Though the use of alcohols 2B and 3A is permissible in analysis, they are not to be recommended for use as solvents for lac used for glazing candies.)

Inasmuch as other constituents of many candies—namely, dextrose, coloring matter, fatty matter, and alkaloids such as theobromine—would be extracted in part or completely, evaporation of the alcoholic extract and subsequent weighing could not be used. Water could be added to precipitate the lac from the alcoholic solution, but the partial formation of colloidal dispersion as well as the precipitation of fats made the method of filtration and weighing impractical. It was then decided to base the determination on the solvent proper-



ties of alkali on the lac acid (11). Sodium carbonate was chosen because it can be used as a primary standard, thus avoiding the need of standardizing its solution. The reaction is (3)



The literature was again consulted to determine the equivalent value of lac in terms of sodium carbonate. Rogers gave 8 as the equivalent (4), while Murty of the Indian Lac Research Institute gave 7.7 (3). To facilitate calculation and titration, a standard solution of sodium carbonate containing 1 mg. per cc. was prepared. Titrations were run on aliquot portions of a weighed sample of pure lac in alcohol 2B. This alcohol and 3A were preferred to alcohol 35 because the denaturant of alcohol 35 reacted slowly with alkali, interfering with the sharpness of the end point.

Phenolphthalein was first used as indicator, but the light purple-red color due to formation of lac dye from chromogen, which is not entirely removed in lac processing, confused the end point (5). Phenol red, which gives a strong red color at a slightly lower pH than phenolphthalein, was found to be a satisfactory indicator. The end point occurs at the point where only sodium shellacate and sodium bicarbonate are in the solution. The first drop of excess sodium carbonate should signify the end point, at the transition pH where phenolphthalein turns red. The color obtained in the titrated solution by adding one drop in excess is too weak to be readily distinguished from the light purple-red produced by the lac dye formation. Titrations on aliquot portions of alcoholic lac solutions, run by the method outlined below, agreed most closely with the factor 8 as being the lac equivalent of one part of sodium carbonate. This is in agreement with Rogers (4) and in close agreement with Murty (3).

The factor as well as the method was further checked by determining the lac content of aliquot samples of glazed candies. Known quantities of lac were added and the total lac content was determined. The difference checked closely with the added charge of lac. Light orange refined lac, such as is used in the candy industry, was used in these tests because of its permanence in this climate. Bleached lac offers a difficulty in its gradual change into an alcohol- and alkali-insoluble form (6). This change cannot be stopped and will take place in time with every bleached lac (6). For this reason candies treated with solutions of bleached lac should be tested promptly.

TABLE I. RECOVERY OF KNOWN QUANTITIES OF LAC

Charge Mg.	Recovered, Using Factor 8 Mg.	Error	
		10 grams of candy %	20 grams of candy %
49.7	49.1	0.006	0.003
50.0	49.2	0.008	0.004
63.3	64.0	0.007	0.004
58.6	58.6	0.000	0.000
36.8	34.2	0.026	0.013
38.2	38.4	0.002	0.001
37.1	37.0	0.001	0.001
37.6	36.4	0.012	0.006

### Method

Fifty grams of candy, glazed with pure lac, are weighed on a quantitative balance, or, since only four significant figures are needed, on a good platform. The candy is covered with alcohol 3A or 2B and allowed to stand with occasional stirring for 1 hour. Generally less than 40 cc. of alcohol are needed. The alcohol is decanted through filter paper into a 50-cc. volumetric flask or into a 100-cc. flask if necessary, 10 cc. more of alcohol are added to the candy, allowed to stand with occasional shaking for 0.5 hour, and decanted through the same filter paper into the same volumetric flask. The candy is washed with sufficient alcohol to bring the alcoholic extract up to volume.

Twenty cubic centimeters of filtrate are transferred to a 125-cc. flask or beaker. If the lac solution has been brought up to

50 cc., the charge taken for titration represents approximately 20 grams of candy; if it has been brought up to 100 cc. the charge is approximately 10 grams. Twenty cubic centimeters of distilled water are added with shaking. The dispersion is brought up to boiling and kept at the boiling point for at least 5 minutes, and 3 to 5 drops of phenol red are added. The lac is titrated while hot with standard sodium carbonate till a deep red is obtained which matches the color formed by adding 1 to 2 drops of the standard solution to a similarly treated 50 per cent alcohol solution which has been kept at the boiling point for at least 5 minutes. Boiling for at least 5 minutes serves two purposes: Sodium carbonate will not dissolve lac in the cold, and it is necessary to boil out carbon dioxide, since it will effect the titration. The number of cubic centimeters of alkali consumed, multiplied by 8, is equal to the number of milligrams of lac in the titrated sample.

TABLE II. RECOVERY OF KNOWN ADDITIONS OF LAC TO GLAZED CANDY

Charge Added Mg.	Predetermined Lac Content of Candy %	Recovery of Added Lac Mg.	Error	
			10 grams of candy %	20 grams of candy %
63.1	0.29	61.9	0.012	0.006
34.8	0.16	34.6	0.002	0.001
28.6	0.24	26.4	0.022	0.011
37.6	0.29	35.2	0.024	0.012
18.4	0.34	17.8	0.006	0.003
18.4	0.34	16.7	0.017	0.009

### Preparation of Solutions

**Standard Sodium Carbonate.** One gram of anhydrous c. p. sodium carbonate is dissolved in 1 liter of freshly boiled distilled water.

**Phenol Red.** In a mortar 0.1 gram of dry phenol red is mixed with 28.2 cc. of 0.01 N sodium hydroxide, and diluted to 250 cc. with distilled water.

### Possible Interferences

Organic acids, particularly citric acid, are present in some candies. When their presence is suspected or in the event of a very high lac figure, it is advisable to titrate a water extract of the candy and deduct the number of cubic centimeters of sodium hydroxide consumed from that needed in the lac titration. Fatty acids can be accounted for by first extracting the acids from the candy with carbon tetrachloride. After evaporation of the solvent the fatty acids can be redissolved in alcohol and after the addition of water, titrated with the standard sodium carbonate, remembering that 6.8 per cent of the lac is soluble in carbon tetrachloride (8). The fatty acid-free candy can then be analyzed for remaining lac content.

In the course of this work, over 250 samples of candy were tested for lac content. In only two instances was it necessary to provide for interferences—namely, citric acid. Though in no case did the authors know the true lac percentage, they feel that the results of analyses run on known quantities of lac and on candies before and after the addition of known quantities of lac have proved the worth of this method.

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# MODERN

# LABORATORIES



## New Chemical Engineering Building at Case School of Applied Science

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**T**HE first unit of the new chemical engineering building at Case School of Applied Science was completed and occupied in October. This unit, comprising about 40 per cent of the total proposed building, houses the laboratories for elementary and advanced chemical engineering, testing of fuels and lubricants, and physical and organic chemistry.

It greatly improves departmental facilities for upper-class and graduate instruction and research, as well as for cooperative industrial research.

The building, designed by Walker and Weeks and built by the Emerson Co., both of Cleveland, is of welded structural steel frame with reinforced concrete floor slabs and brick facing. It is of the modern industrial type, the horizontal lines being accentuated by continuous rows of full-length windows. The building is three stories high with a half-submerged basement. At the south end an annex, with floor at the basement level and ceiling at the ceiling level of the first floor, furnishes headroom for erecting towers and other tall apparatus.

At the floor level of the first floor, easily removable subway grating is laid over the I-beams to form a balcony. In one corner of the annex, four concrete shelters have been built behind which high-pressure reactions can be carried on. All controls and gages for such studies are brought through a heavy steel plate in the front of the shelter.

The fact that this unit is a part of a building to be ultimately finished has dictated in some measure the location of stairways and interconnecting hallways and materials of construction. Every effort has been made to obtain all essential facilities at a minimum expenditure. The cost of construction, not including laboratory furniture, was about 45 cents per cubic foot as compared with an average of 35 cents for an ordinary industrial building of comparable size.

The entire building is wired for 110- and 220-volt alternating current. All electrical circuits are equipped with circuit breakers instead of fuses. The 220-volt single- and three-phase circuits are used for operating machinery, while the 110-volt circuit is reserved for lighting and other minor uses. For



UNIT OPERATIONS LABORATORY, SHOWING SERVICE RACKS FOR MOUNTING CHEMICAL ENGINEERING EQUIPMENT



steady voltage, current is obtained from one of two storage battery sets—one bank of 120 ampere-hour capacity at 32 volts and one of 240 ampere-hours at 4 volts—and is distributed to outlets from a standard plug panel board.

Lighting is provided in the laboratories in the basement and first two floors by standard fixtures using a bowl-type diffusing unit and an enameled steel reflector. The offices, corridors, class rooms, and third floor are lighted only by the glass diffusing unit without a reflector. This provides an illumination of about 25 foot-candles at the desk top. Under the balcony in the annex fluorescent tubular lamps in trough reflectors provide illumination without glare.

General heating is provided by steam radiators and fresh air for ventilation is supplied by unit heaters, all thermostatically controlled. To obtain even distribution and prevent dead-air pockets in the large first-floor laboratory, the air supply is furnished by a heater and blower unit situated on the roof of the annex and is distributed by Transite ducts through louvered openings. The hoods along with auxiliary ducts serve in part to carry off the used air. By this system, the air in the large laboratories is changed about fifteen times per hour and throughout the rest of the building about ten.

All motors and fans used for the fume hood systems are contained in a penthouse on the roof, but the control switch is located at the hood. These switches are of the magnetic type with a small pilot lamp in the circuit which is lighted when the fan is in operation. The main switch is pulled for a moment at the close of each day, shutting off all fans.

The automatic distilled water system is located in the penthouse, where live steam is scrubbed, condensed in block tin, and stored in an acidproof 120-gallon stoneware jar. The cover is fitted with a float that automatically stops the flow of steam when the jar is full and starts it again when needed. From this jar, water is distributed by pure aluminum lines with all-aluminum snap faucets in the laboratories.

The basement is an entire unit for the study of chemical engineering unit operations. This group is composed of a large general laboratory running lengthwise, flanked on the north by a group of small laboratories devoted to the study of special operations and on the south by the annex.

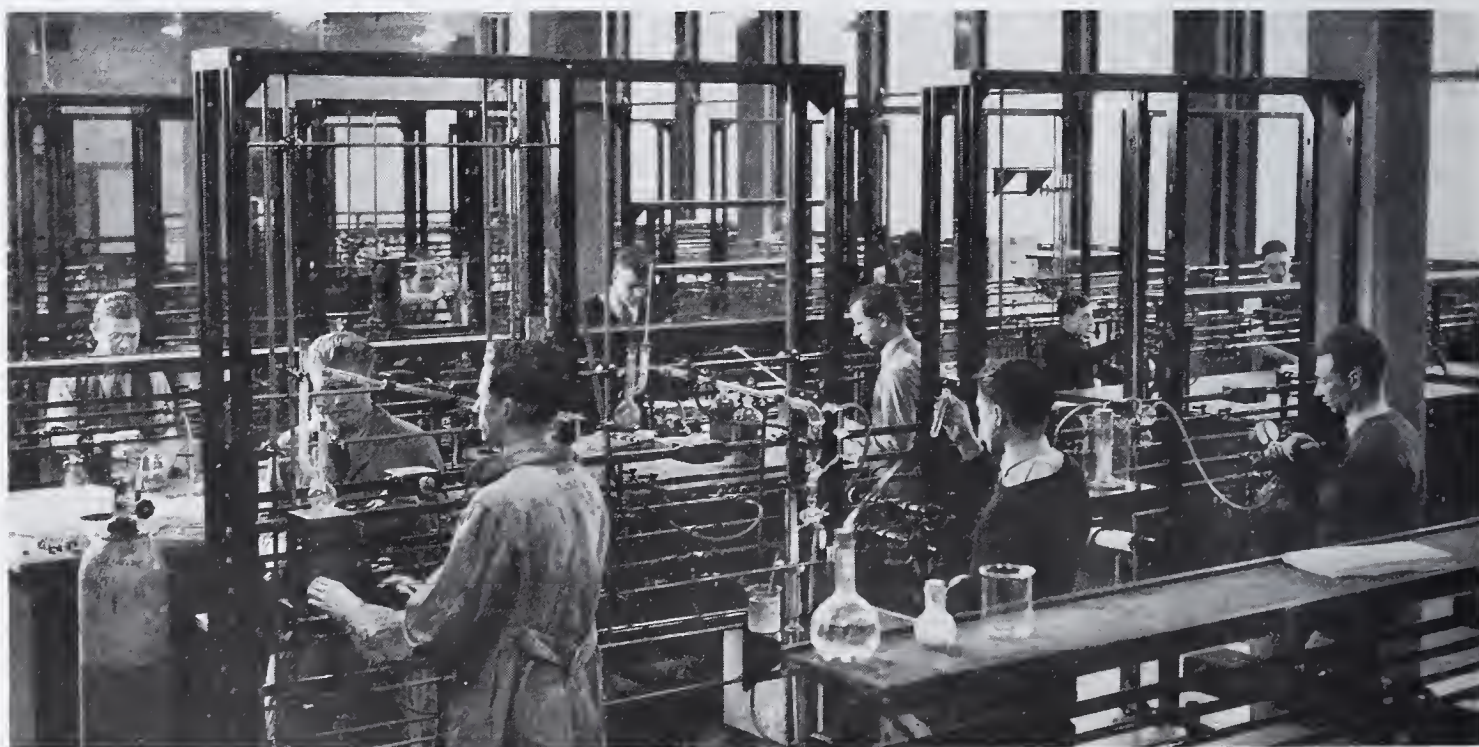
The large laboratory is provided with three drain troughs approximately 60 feet long and spaced 9 feet from center to

center to provide drainage for any equipment set up over them. To facilitate the mounting of equipment sixteen racks 3 feet long and 5 feet high, made of 2-inch pipe, are mounted over the drain troughs. To each rack are piped 15- and 110-pound steam, gas, water, and air with shutoff valves at the racks. Switches and outlet plugs at each end of the rack provide 110-volt single-phase electric power. Around these racks equipment for research and instruction in fluid flow, meter calibrations, heat transfer, evaporation, mixing, filtration, centrifugal separation, etc., may be set up.

The study of grinding and classification is confined to a small laboratory at the north end because of the dust problem. Similarly, owing to the need of even temperature, another small laboratory at the north end contains the equipment for the study of drying. A storeroom and balance room and an office with a connecting private laboratory make up this group. At the south end, the laboratory opens into the annex where heavier equipment and apparatus requiring more than average headroom may be set up to study distillation, adsorption, spray drying, and similar unit operations.

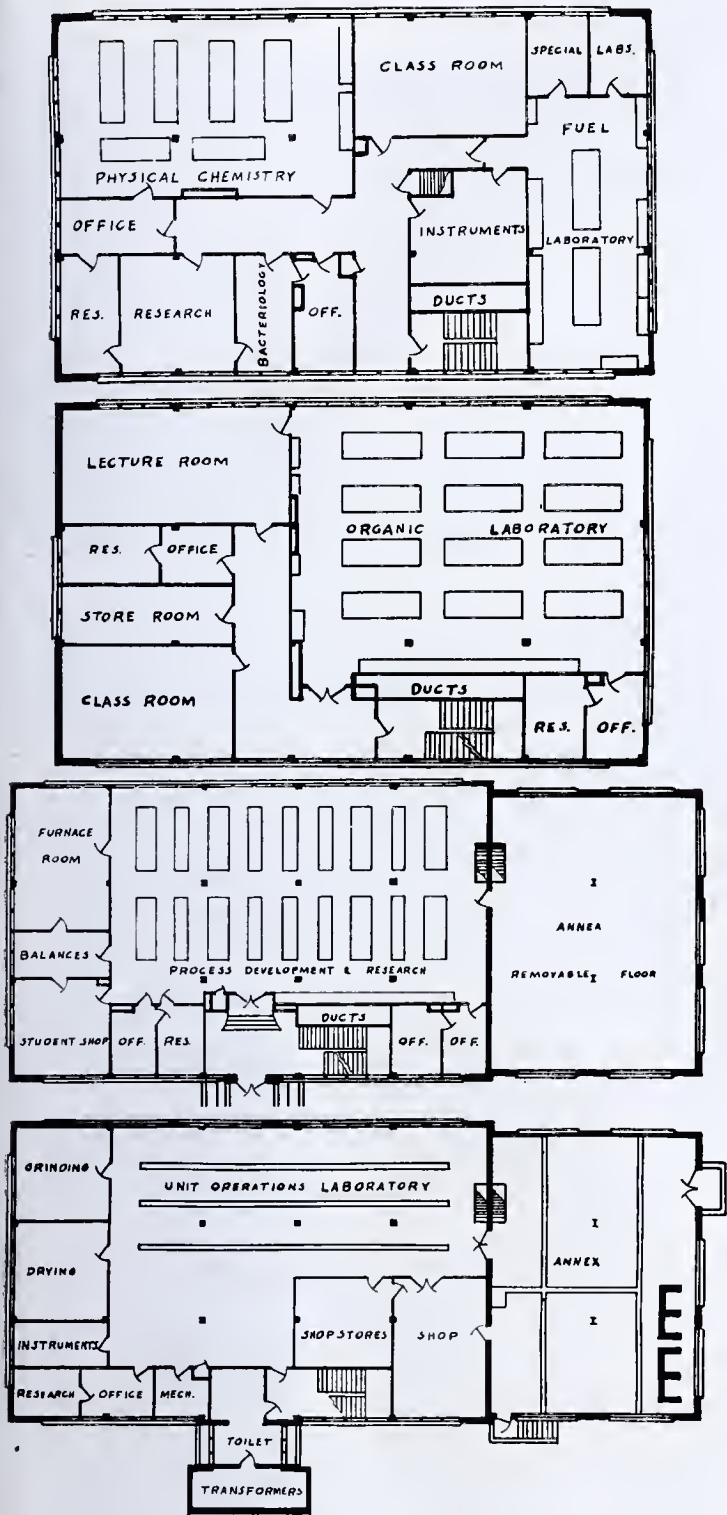
For easy accessibility from the unit operations laboratory, the mechanic's shop and mechanical storeroom are located in the basement. The storeroom is outfitted with bins and shelves for pipe, rods, angle iron, pipe fittings, spare pumps, motors, and miscellaneous engineering supplies. For repairs and construction of new equipment and special apparatus the shop is equipped with a 13-inch swing 6-foot bed screw-feed lathe, floor-stand drill press, 12-inch grinding wheel, milling machine, power saw, and ample work bench space.

The first floor is designed to give maximum flexibility and to furnish all the common facilities required for small-scale industrial research and process development work. For this reason, the main laboratory is flanked on the north by three small rooms, the first of which is a room for high-temperature research, equipped with a gas-fired muffle furnace and two gas-fired crucible furnaces. For calibration of thermal measuring equipment, ignition of samples, and high-temperature research four electric crucible furnaces, an electric muffle furnace, a Globar heated muffle, and a similarly heated tube furnace are provided. The Globar furnaces are equipped with temperature-recording and control equipment. In the second room, equipment for glass blowing, pipe fitting, and light metal



LABORATORY FOR RESEARCH AND PROCESS DEVELOPMENT, SHOWING TYPE OF DESK FOR ERECTING APPARATUS





work is provided in a student shop, so that the students may construct equipment needed in research and pilot-plant work. The third room is used as a balance room and instrument storeroom to service the main laboratory.

The south end of the main laboratory opens onto the balcony in the annex, where bulky equipment may be set up.

Eight standard center tables provide locker space for 64 students in two groups. For semipermanent equipment for industrial research and process development 8 special tables are installed. Two tables 3 feet wide, 6 feet long, and 20 inches high separated by an Alberene stone sink  $36 \times 18 \times 12$  inches deep constitute a unit. Lengthwise along the center is a double-faced rack 7 feet high divided into two 3-foot sections over each table. Keyhole slots placed on 6-inch centers are located in the vertical channels and top plate, so that a lattice of rods can be installed to support special equipment. Service lines for low-pressure steam, air, gas, water, and electricity are located in the racks in the center line of the table; high-pressure steam lines are provided at the floor to be carried into the racks as required. To remove fumes that cannot be easily absorbed, a suction line with snap closure top is placed on each rack, connecting through Transite pipe to

a blower in the penthouse. Each outlet can remove 25 cubic feet of gas per minute when all are opened.

In the center of the room are two tables for mounting two drying ovens, a centrifuge, and automatic burets with standard solutions for general use. On the standard-type desks distillation columns for analytical and semiplant-scale separations can be mounted, with equipment for measuring vapor pressure, melting points, and liquid-vapor compositions of materials.

The second floor organic laboratory has 10 center tables, duplicates of those in the senior laboratory, with lockers for 80 men. On the center tables are individual steam cones for distillations, and special stainless steel supports, replacing ring stands, which slide back under the reagent racks when not in use. A pair of tables and sink and a low distillation rack, duplicating those in the center of the senior laboratory, are also provided.

Laboratories for physical chemistry, fuels, water, and lubricants research, and bacteriology are provided on the third floor, as well as a room for the storage and dispensing of instruments to service these departments.

The physical chemistry laboratory is equipped with a balance table, six flat-top double center tables, and a furnace table, with two electrical furnaces for thermal analysis and an 8-foot wall table with locked cupboards, services, and end sink. The services on the center tables are gas, water, 110-volt alternating current electric power, and constant-voltage current. The direct current is distributed to outlets on the center tables and to three other small laboratories from a distribution board in the physical chemistry laboratory. Through a system of jacks, plugs, and cords voltages are provided in 2-volt steps, from 2 to 32 volts, to any outlet on the system from the panel referred to above.

The fuels, lubricants, and water laboratory is allotted a space 20 by 60 feet, one end of which is divided into two smaller rooms. One of these small rooms is used for calorimetric measurements on solid, liquid, and gaseous fuels while the other is outfitted for bacteriological examination of water.

In the main laboratory are two center tables, 12 feet long and 4.5 feet wide, with an end sink and three 6-inch drain cups. Service for gas, steam, water, and electric power is supplied in pipes in the reagent racks. The lower sections consist of 72 locked drawers, about 12 inches square on the front and 20 inches deep, for student samples and glassware. Three 8-foot tables and one 6-foot table hold gas-analysis equipment, an electric oven, and an electric muffle furnace. One open-front hood is equipped with two 6-place steam baths, water, steam, gas, electricity, and a 6-inch hemispherical drain cup. There are six closed-front hoods, four 3 feet wide and two 4.5 feet wide, primarily for permanent installation of special equipment for fuel or lubricant analysis requiring limited fume removal. The understructure is composed of steel cupboards for general storage. All cupboards and sash are supplied with locks.

The building provides seven offices for the staff, each with a connecting private research laboratory of similar size. There are also two recitation rooms and a lecture room large enough for 60 students and a lecture demonstration table.

The laboratory furniture is lead-coated copper-bearing steel finished in olive green acid-resisting enamel, with the exception of the physical chemistry laboratory, where existing oak tables were used and additional equipment was purchased to match. The center tables for the senior, organic, and research laboratories were assembled from a single basic unit.

Electricity, water, gas, and low-pressure steam are provided in the reagent rack, with all fittings of black oxidized brass. All chemical drains are acid-resisting high-silicon iron, and two 6-inch hemispherical sinks are placed under the reagent rack on each side of the sink.

The hoods in the senior and organic laboratories are open front of a modified Cornel type. The superstructure of all hoods is a standard construction of impregnated Transite set in a reinforcing frame of lead-coated steel. Steam, gas, water, and electrical services are supplied in each hood with remote controls through the apron in front.

All piping is exposed under the ceilings, with the vertical risers in the fume duct shaft, so that if repairs are required or extensions desired all lines are easily accessible.



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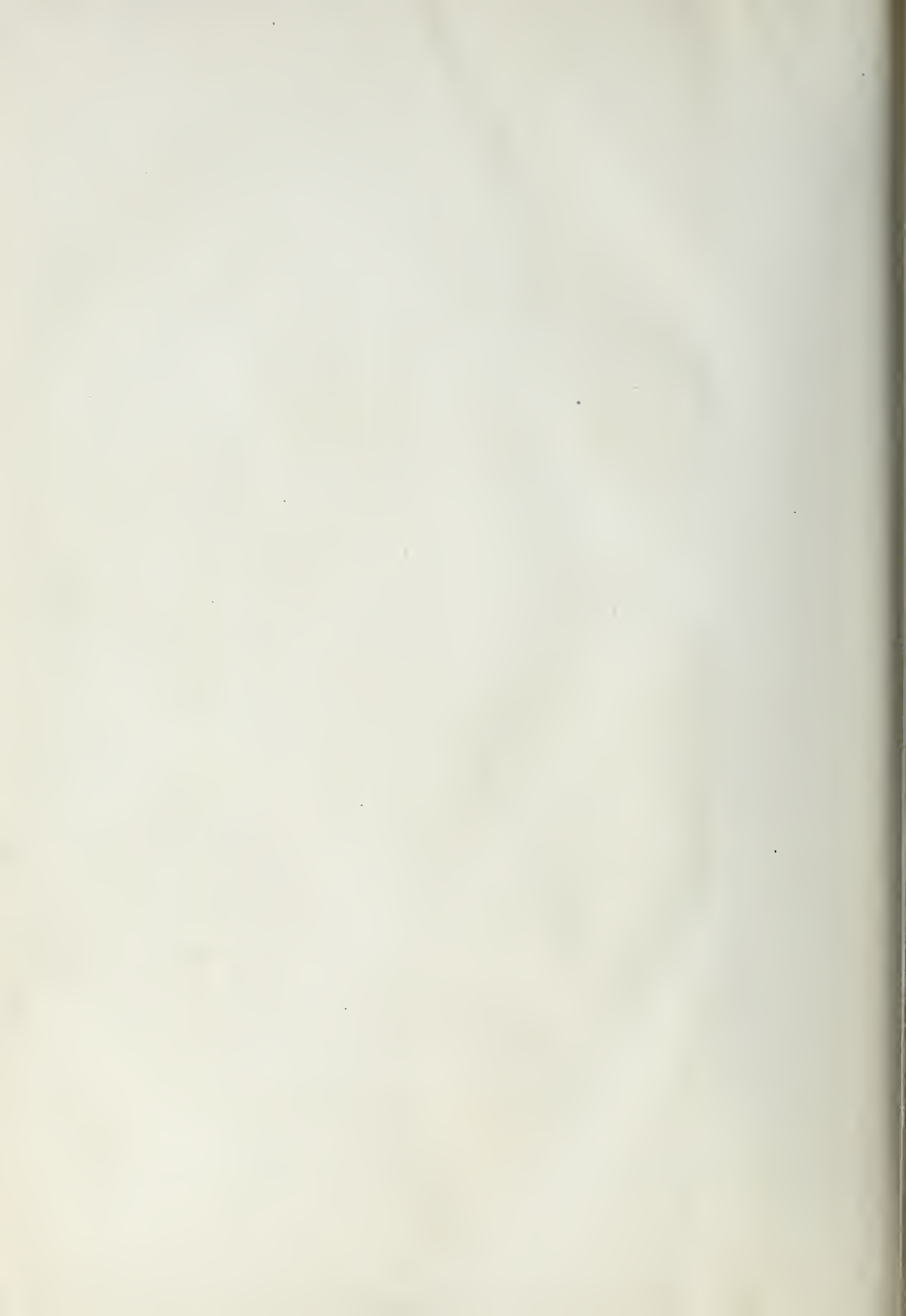


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